8/18/00

COMPOSITION FOR DYEING KERATINOUS FIBRES WITH A CATIONIC DIRECT DYE AND A QUATERNARY AMMONIUM SALT

The invention relates to a composition for dyeing keratinous fibres, in particular human keratinous fibres such as hair, comprising, in an appropriate dyeing medium, at least one cationic direct dye of a given formula, and at least one quaternary ammonium salt.

The subject of the invention is also the dyeing methods and devices using the said composition.

In the hair domain, it is possible to distinguish two types of dyeing.

The first is the semipermanent or temporary dyeing, or direct dyeing, which involves dyes capable of bringing the natural colour of the hair a more or less marked colour modification which is resistant, where appropriate, to several shampooings. These dyes are called direct dyes; they can be used with or without oxidizing agent. In the presence of oxidizing agent, the aim is to obtain a lightening dyeing. Lightening dyeing is performed by applying to the hair the fresh mixture of a direct dye and of an oxidizing agent and makes it possible in particular to obtain, by lightening of the melanin of the hair, an advantageous effect such as a uniform colour in the case of grey hair or to make the colour stand out in the case of naturally pigmented hair.

The second is permanent dyeing or oxidation dyeing. The latter is performed with so-called "oxidation" dyes comprising oxidation dye precursors and couplers. The oxidation dye precursors, commonly called "oxidation bases" are compounds which are initially colourless or faintly coloured which develop their dyeing power inside the hair in the presence of oxidizing agents added at the time of use, leading to the formation of coloured and dyeing compounds. The formation of these coloured and dyeing compounds results either from an oxidative condensation of the "oxidation bases" with themselves, or an oxidative condensation of the "oxidation bases" with colour modifying compounds commonly called "couplers" and generally present in the dyeing compositions used in oxidation dyeing.

To vary the shades obtained with the said oxidation dyes, or to increase their shimmer, direct dyes are sometimes added to them.

Among the cationic direct dyes available in the field of dyeing of keratinous fibres, especially human keratinous fibres, compounds are already known whose structure is developed in the text which follows; nevertheless, these dyes lead to colours which exhibit characteristics which are still inadequate from the point of view of the intensity and homogeneity of the colour distributed along the fibre; it is said, in this case, that the colour is too selective, and from the

point of view of fastness, in terms of resistance to various attacks to which the hair may be subjected (light, adverse weather conditions, shampooings).

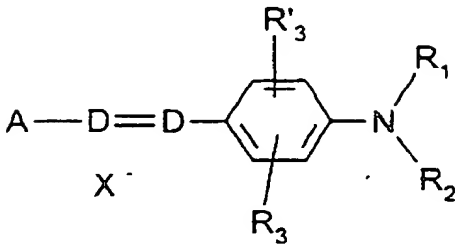
However, after major research studies carried out on this question, the applicant has just now discovered that it is possible to obtain novel compositions for dyeing keratinous fibres which are capable of giving intense and only slightly selective colours which are quite resistant nevertheless to the various attacks to which the hair may be subjected, by combining at least one ~~particular anionic surfactant~~ quaternary ammonium salt with at least one cationic direct dye known in the prior art and which have the respective formulae defined hereinafter.

This discovery forms the basis of the present invention.

The first subject of the present invention is therefore a composition for dyeing keratinous fibres and in particular human keratinous fibres such as hair, containing in an appropriate dyeing medium, **(i)** at least one cationic direct dye whose structure corresponds to the formulae (I) to (IV) defined hereinafter, characterized in that it contains in addition **(ii)** at least one quaternary ammonium salt.

(i) The cationic direct dye which can be used according to the present invention is a compound chosen from those of the following formulae (I), (II), (III), (III'), (IV):

a) the compounds of the following formula (I):



(I)

in which:

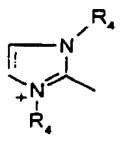
D represents a nitrogen atom or the -CH group,

R_1 and R_2, which are identical or different, represent a hydrogen atom; a C_1-C_4 alkyl radical which may be substituted with a -CN, -OH or $-NH_2$ radical or form with a carbon atom of the benzene ring an optionally oxygen-containing or nitrogen-containing heterocycle which may be substituted with one or more C_1-C_4 alkyl radicals; a 4'-aminophenyl radical,

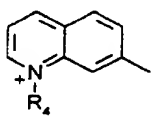
R_3 and R'_3, which are identical or different, represent a hydrogen or halogen atom chosen from chlorine, bromine, iodine and fluorine, a cyano, C_1-C_4 alkyl, C_1-C_4 alkoxy or acetyloxy radical,

X^- represents an anion which is preferably chosen from chloride, methylsulphate and acetate,

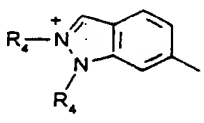
A represents a group chosen from the following structures A_1 to A_{19}:



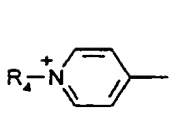
A_1 ;

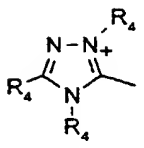


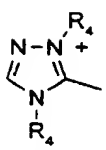
A_2 ;

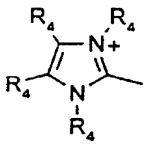


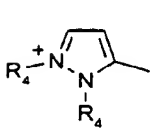
A_3 ;

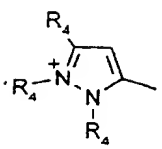

A_4

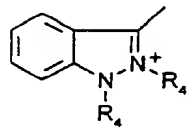

A_5

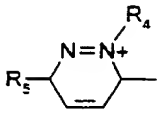

A_6

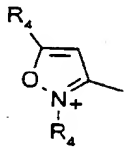

A_7

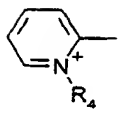

A_8

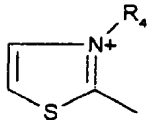

A_9

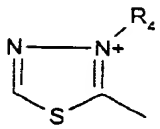

A_{10}

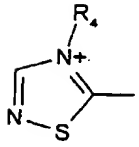

A_{11}

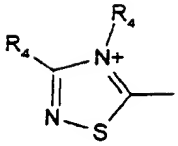

A_{12}

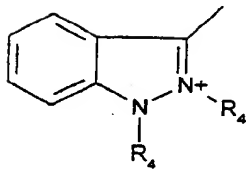

A_{13}


A_{14}

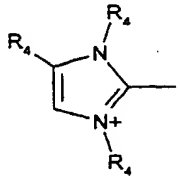

A_{15}


A_{16}


A_{17}


A_{18}

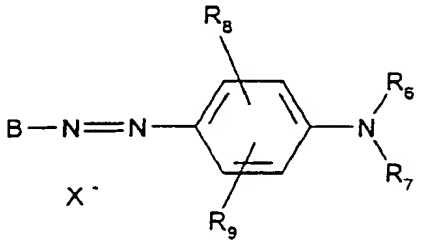
and


A_{19} ;

in which R_4 represents a C_1-C_4 alkyl radical which may be substituted with a hydroxyl radical and R_5 represents

a C_1-C_4 alkoxy radical, with the proviso that when D represents -CH, A represents A_4 or A_{13} and R_3 is different from an alkoxy radical, then R_1 and R_2 do not simultaneously denote a hydrogen atom;

b) the compounds of the following formula (II):



(II)

in which:

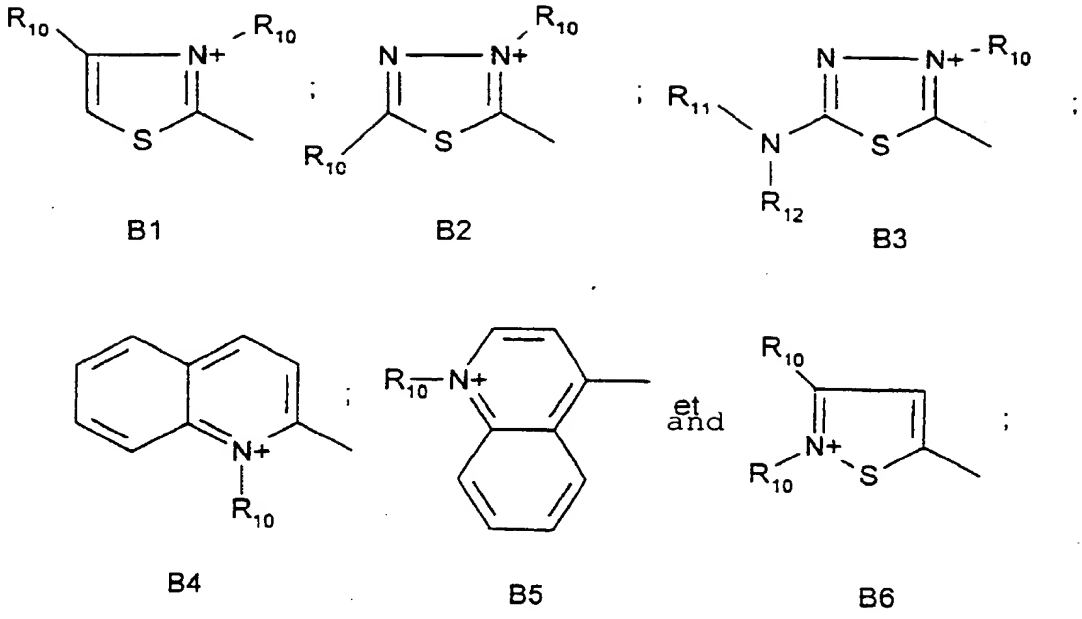
R_6 represents a hydrogen atom or a C_1-C_4 alkyl radical,

R_7 represents a hydrogen atom, an alkyl radical which may be substituted with a -CN radical or with an amino group, a 4'-aminophenyl radical or forms with R_6 an optionally oxygen-containing and/or nitrogen-containing heterocycle which may be substituted with a C_1-C_4 alkyl radical,

R_8 and R_9 , which are identical or different, represent a hydrogen atom, a halogen atom such as bromine, chlorine, iodine or fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical, a -CN radical,

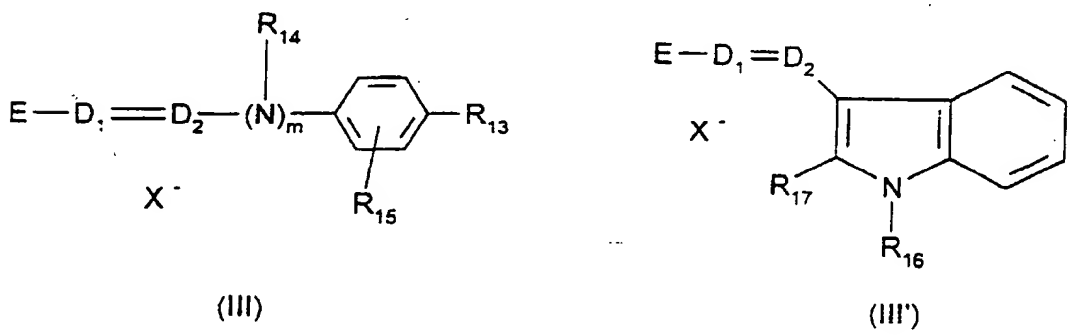
X^- represents an anion which is preferably chosen from chloride, methylsulphate and acetate,

B represents a group chosen from the following structures B1 to B6:



in which R_{10} represents a C_1-C_4 alkyl radical, R_{11} and R_{12}, which are identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical;

c) the compounds of the following formulae (III) and (III'):



in which:

R_{13} represents a hydrogen atom, a C_1-C_4 alkoxy radical, a halogen atom such as bromine, chlorine, iodine or fluorine or an amino radical,

R_{14} represents a hydrogen atom, a C_1-C_4 alkyl radical or forms with a carbon atom of the benzene ring a heterocycle which is optionally oxygen-containing and/or substituted with one or more C_1-C_4 alkyl groups,

R_{15} represents a hydrogen or halogen atom such as bromine, chlorine, iodine of fluorine,

R_{16} and R_{17}, which are identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical,

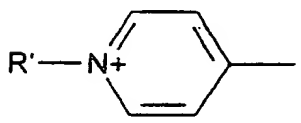
D_1 and D_2, which are identical or different, represent a nitrogen atom or the -CH group,

m = 0 or 1,

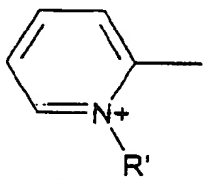
it being understood that when R_{13} represents an unsubstituted amino group, then D_1 and D_2 simultaneously represent a -CH group and m = 0,

X^- represents an anion which is preferably chosen from chloride, methylsulphate and acetate,

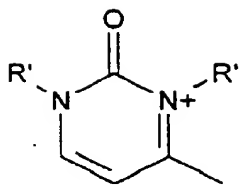
E represents a group chosen from the following structures E1 to E8:



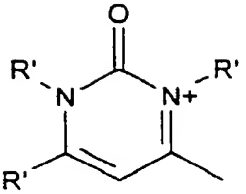
E1 ;



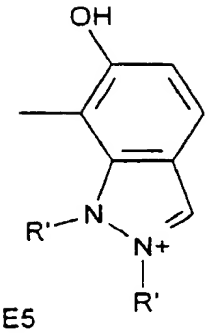
E2 ;



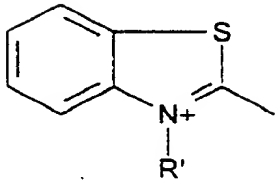
E3



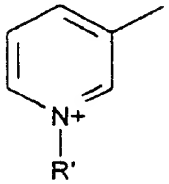
E4



E5

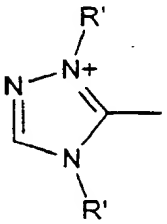


E6



E7

et and

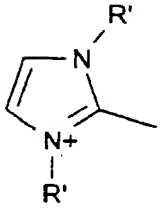


E8

in which R′ represents a C_1-C_4 alkyl radical;

when m = 0 and D_1 represents a nitrogen atom, then E may also denote a group having the following structure E9:

E9



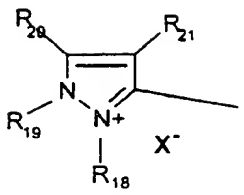
in which R′ represents a C_1-C_4 alkyl radical,

d) the compounds of the following formula (IV):

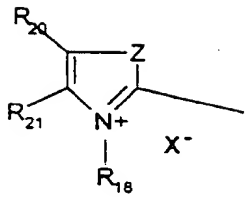
(IV)

in which:

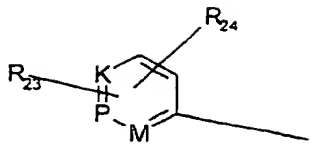
the symbol G represents a group chosen from the following structures G_1 to G_3:



G_1



G_2



G_3

in which structures G_1 to G_3,

R_{18} denotes a C_1-C_4 alkyl radical, a phenyl radical which may be substituted with a C_1-C_4 alkyl radical or a halogen atom chosen from chlorine, bromine, iodine and fluorine;

R_{19} denotes a C_1-C_4 alkyl radical or a phenyl radical;

R_{20} and R_{21}, which are identical or different, represent a C_1-C_4 alkyl radical, a phenyl radical, or form together in G_1 a benzene ring which is substituted with one or more C_1-C_4 alkyl, C_1-C_4 alkoxy or NO_2 radicals, or form together in G_2 a benzene ring which is optionally substituted with one or more C_1-C_4 alkyl, C_1-C_4 alkoxy or NO_2 radicals;

R_{20} may denote, in addition, a hydrogen atom;

Z denotes an oxygen or sulphur atom or an $-NR_{19}$ group;

M represents a group -CH, -CR (R denoting C_1-C_4 alkyl), or $-NR_{22}(X^-)_r$;

K represents a group -CH, -CR (R denoting C_1-C_4 alkyl), or $-NR_{22}(X^-)_r$;

P represents a group -CH, -CR (R denoting C_1-C_4 alkyl), or $-NR_{22}(X^-)_r$; r denotes zero or 1;

R_{22} represents an O^- atom, a C_1-C_4 alkoxy radical or a C_1-C_4 alkyl radical;

R_{23} and R_{24}, which are identical or different, represent a hydrogen or halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl radical, a C_1-C_4 alkoxy radical or an $-NO_2$ radical;

X^- represents an anion which is preferably chosen from chloride, iodide, methylsulphate, ethylsulphate, acetate and perchlorate;

with the proviso that

if R_{22} denotes O^-, then r denotes zero;

if K or P or M denote $-N-(C_1$-C_4 alkyl$)X^-$, then R_{23} or R_{24} is different from a hydrogen atom;

if K denotes $-NR_{22}(X^-)_r$, then M = P = -CH, -CR;

if M denotes $-NR_{22}(X^-)_r$, then K = P = -CH, -CR;

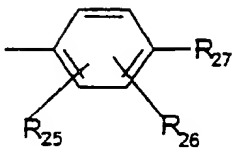
if P denotes $-NR_{22}(X^-)_r$, then K = M and denote -CH or -CR;

if Z denotes a sulphur atom with R_{21} denoting C_1-C_4 alkyl, then R_{20} is different from a hydrogen atom;

if Z denotes $-NR_{22}$ with R_{19} denoting C_1-C_4 alkyl, then at least one of the R_{18}, R_{20} or R_{21} radicals of the group having the structure G_2 is different from a C_1-C_4 alkyl radical;

the symbol J represents:

-(a) a group having the following structure J_1:



J_1

in which structure J_1,

R_{25} represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl radical, a C_1-C_4 alkoxy radical, a radical -OH, $-NO_2$, $-NHR_{28}$, $-NR_{29}R_{30}$, $-NHCO(C_1-C_4alkyl)$, or forms with R_{26} a 5- or 6-membered ring containing or otherwise one or more heteroatoms chosen from nitrogen, oxygen or sulphur;

R_{26} represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical, or forms with R_{27} or R_{28} a 5- or 6-membered ring containing or otherwise one or more heteroatoms chosen from nitrogen, oxygen or sulphur;

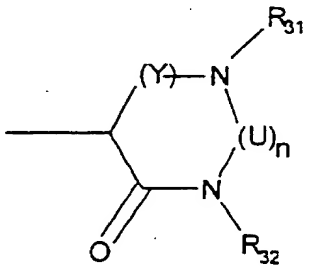
R_{27} represents a hydrogen atom, an -OH radical, an $-NHR_{28}$ radical, an $-NR_{29}R_{30}$ radical;

R_{28} represents a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a phenyl radical;

R_{29} and R_{30}, which are identical or different, represent a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical;

-(b) a 5- or 6- membered nitrogen-containing heterocycle group which is capable of containing other heteroatoms and/or carbonyl-containing groups and which may be substituted with one or more C_1-C_4 alkyl, amino or phenyl radicals,

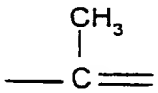
and in particular a group having the following structure J_2:



J_2

in which structure J_2,

R_{31} and R_{32}, which are identical or different, represent a hydrogen atom, a C_1-C_4 alkyl radical, a phenyl radical;

Y denotes the -CO- radical or the radical 

;

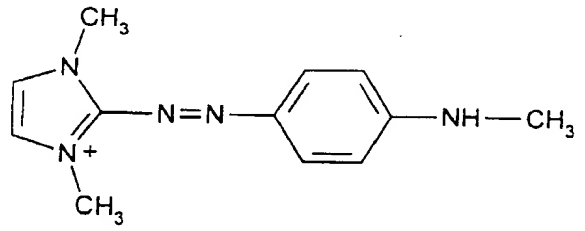
n = 0 or 1, with, when n denotes 1, U denotes the -CO- radical.

In the structures (I) to (IV) defined above, the C_1-C_4 alkyl or alkoxy group preferably denotes methyl, ethyl, butyl, methoxy or ethoxy.

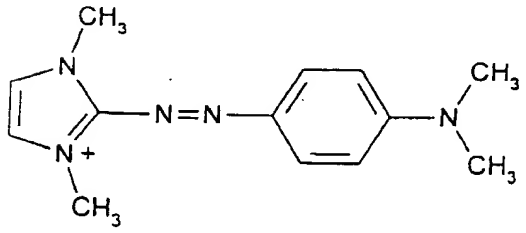
The cationic direct dyes of formulae (I), (II), (III) and (III') which can be used in the dyeing compositions in accordance with the invention are known compounds which are described, for example, in patent applications WO 95/01772, WO 95/15144 and

EP-A-O 714 954. Those of formula (IV) that are useable in the dye compositions of the invention are identified compounds described in, for example, the patent applications FR-2189006, FR-2285851, and FR-2140205 and their certificates of addition.

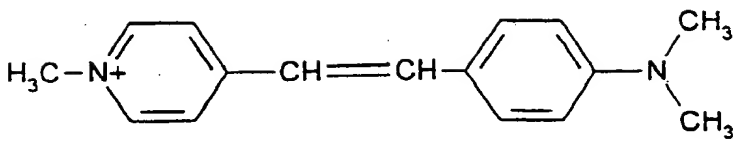
Among the direct cationic dyes of formula (I) that are useable in the dye compositions of the invention, the compounds based on the following structures (I1) to (I54) can be specifically noted.



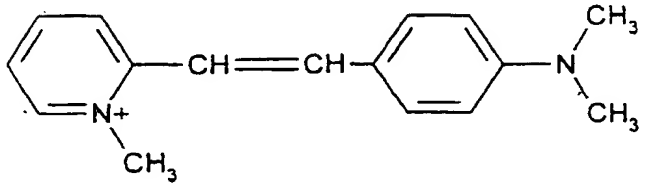
(I1)



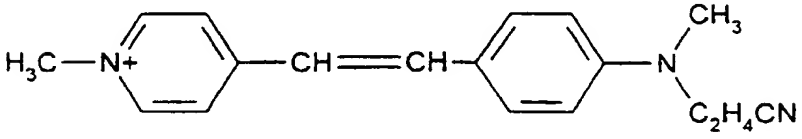
(I2)



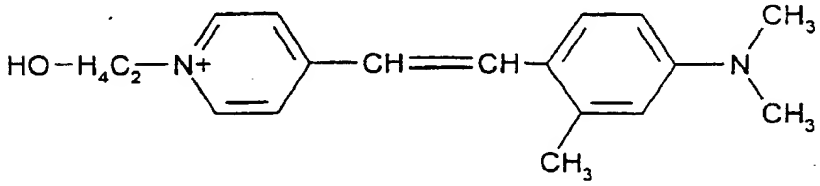
Cl^- (13)



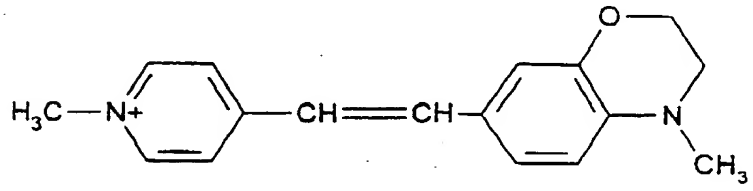
Cl^- (14)



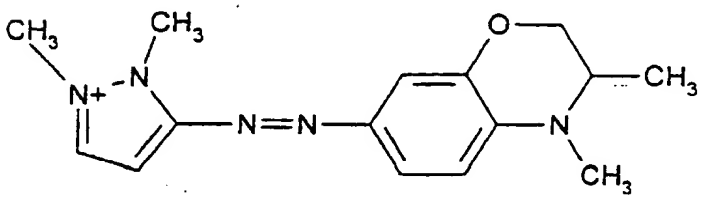
Cl^- (15)



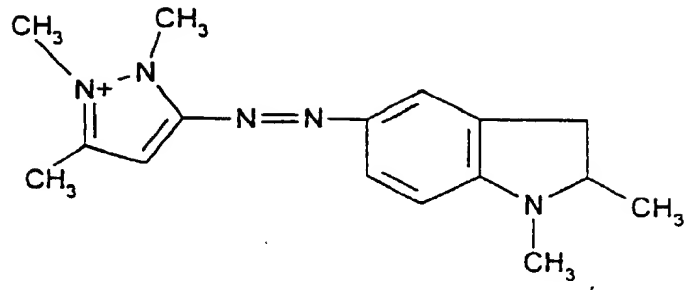
Cl^- (16)



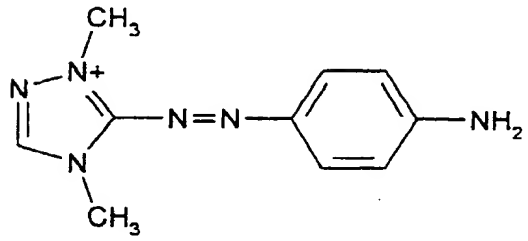
Cl^- (17)



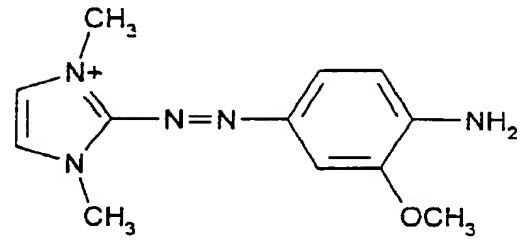
Cl^- (18)



Cl^- (I9)



Cl^- (I10)



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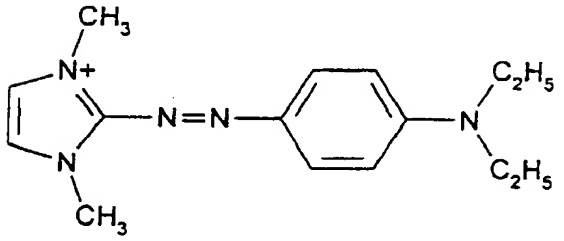

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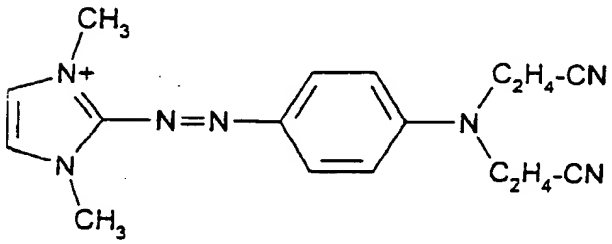

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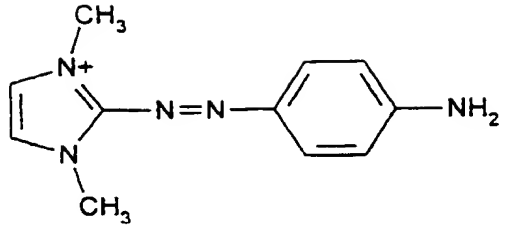

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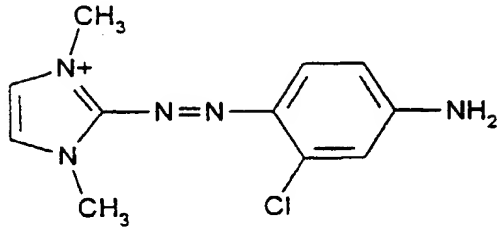

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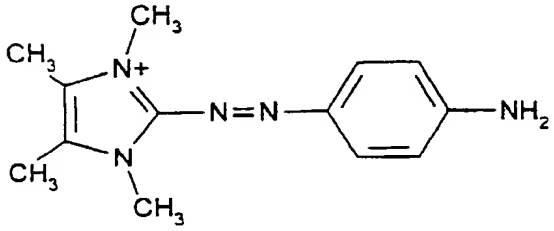

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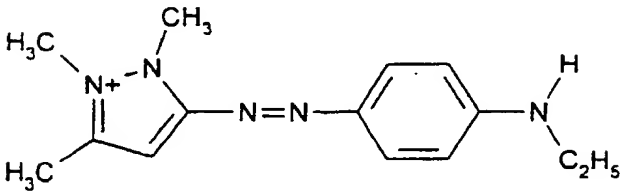
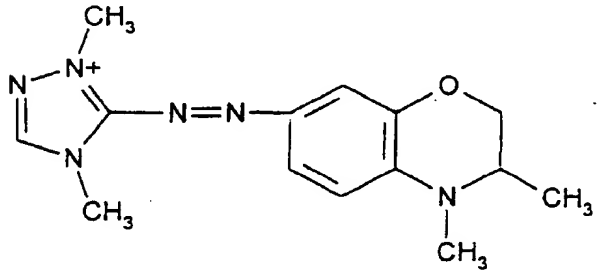
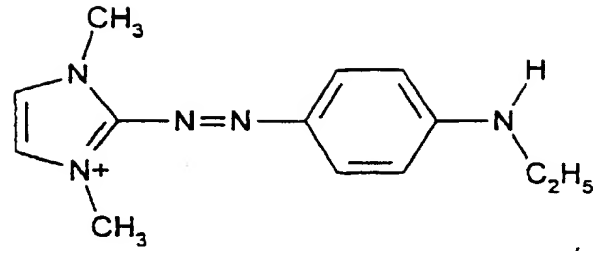


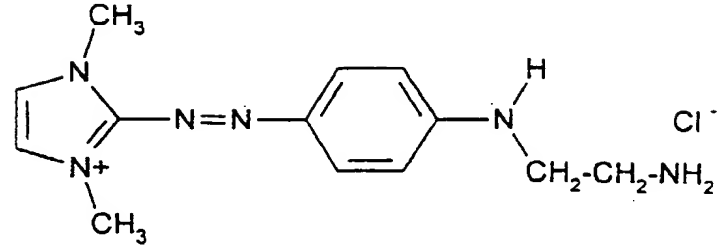
Cl^- (I17)



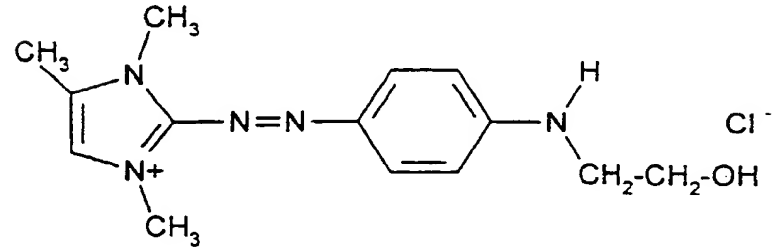
Cl^- (I18)



(I19)



(I20)



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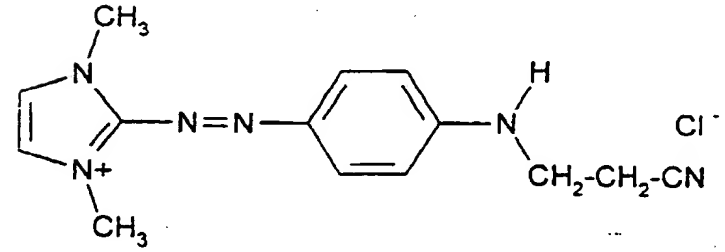
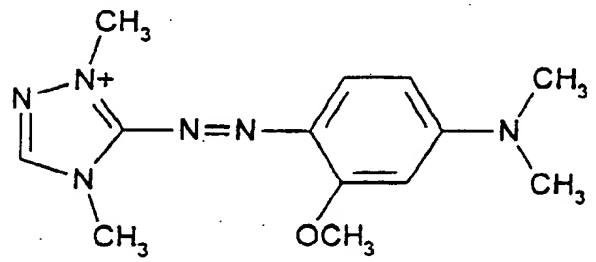
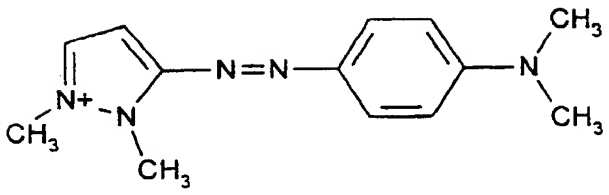


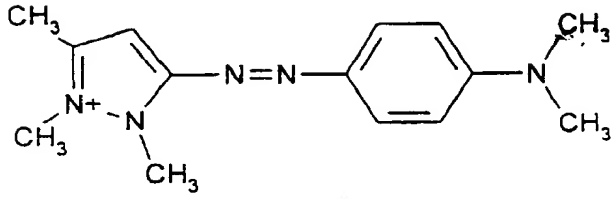
(I22)



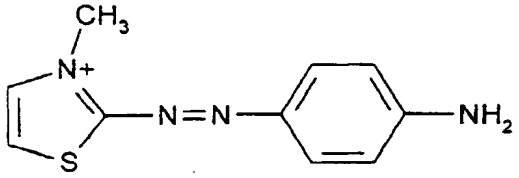
(I23)



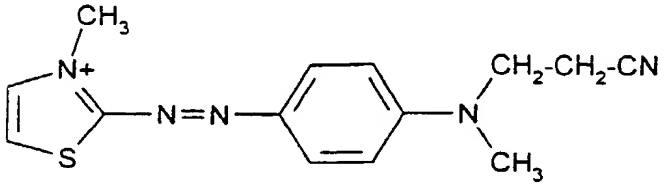
Cl⁻ (I24)



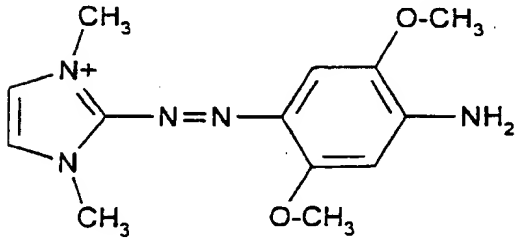
Cl⁻ (I25)



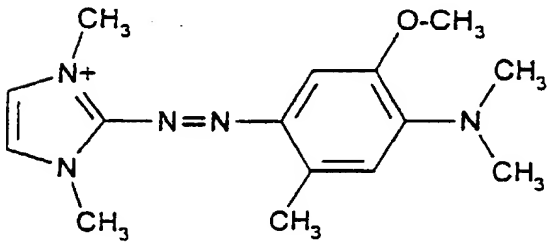
Cl⁻ (I26)



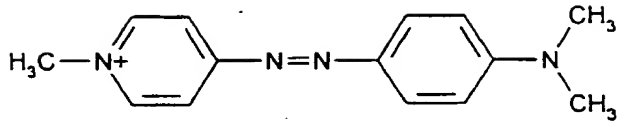
Cl⁻ (I27)



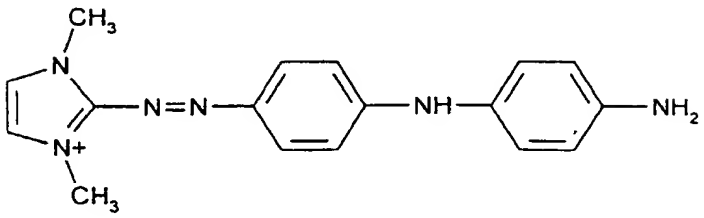
Cl⁻ (I28)



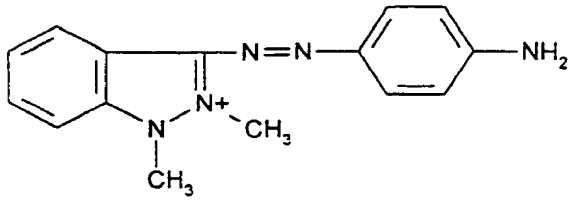
Cl⁻ (I29)



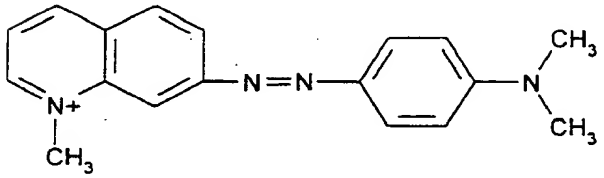
(I30)



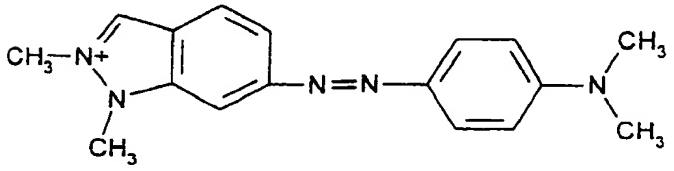
(I31)



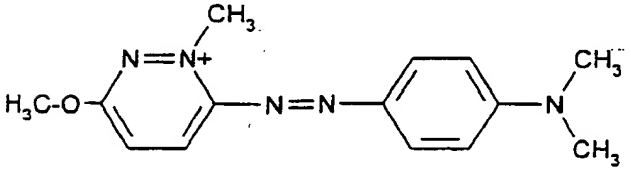
(I32)



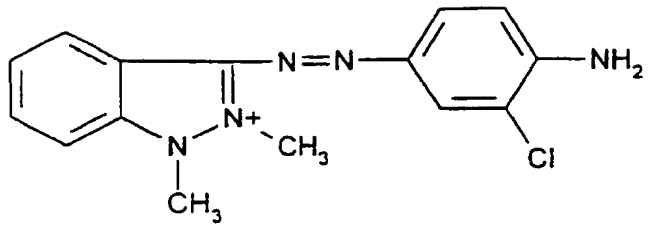
(I33)



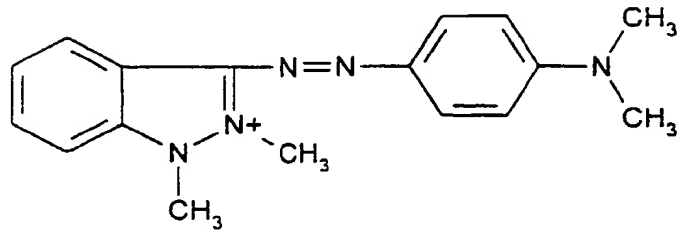
(I34)



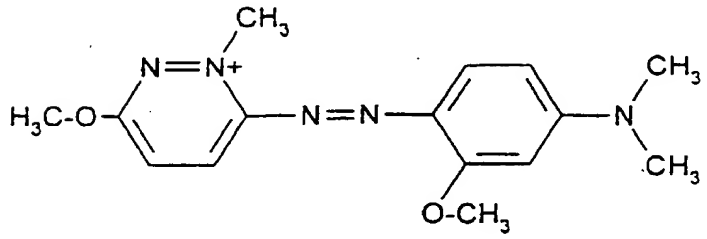
(I35)



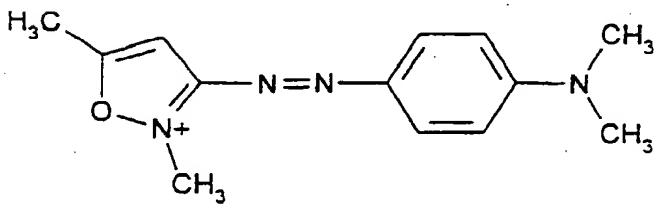
Cl^- (136)



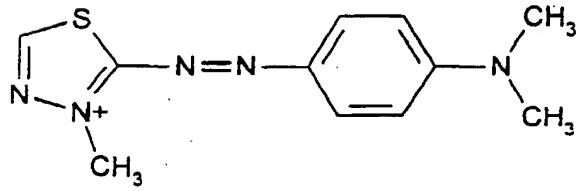
Cl^- (137)



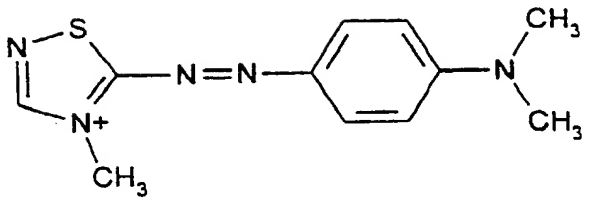
Cl^- (138)



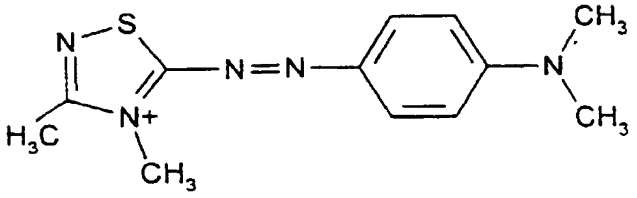
Cl^- (139)



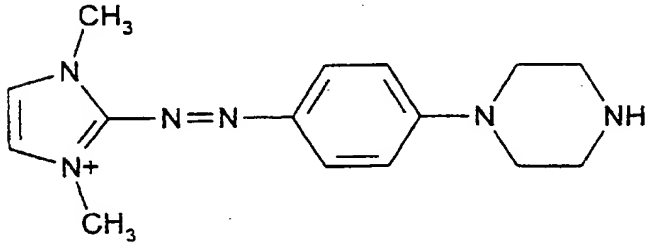
Cl^- (140)



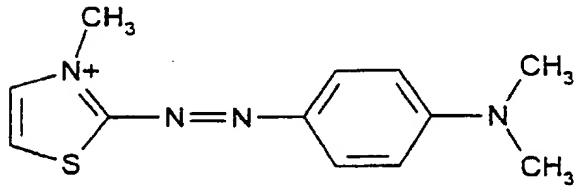
Cl⁻ (141)



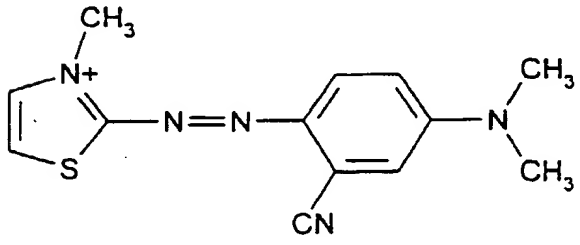
Cl⁻ (142)



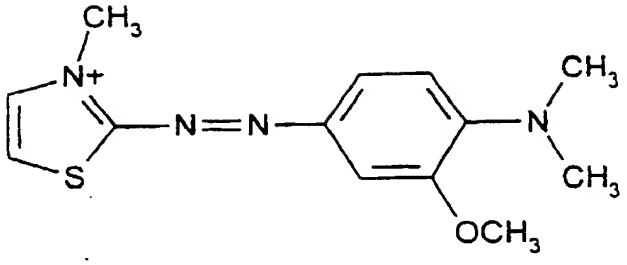
Cl⁻ (143)



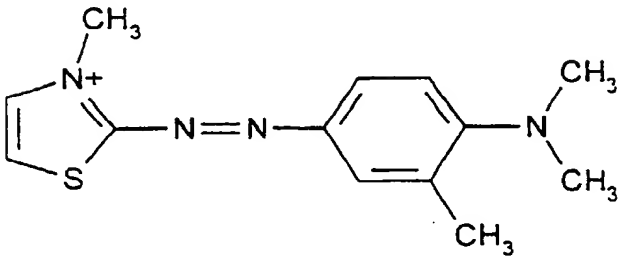
Cl⁻ (144)



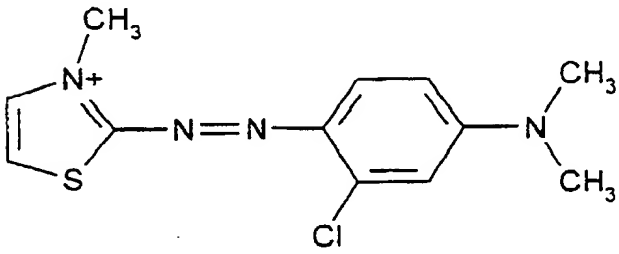
Cl⁻ (145)



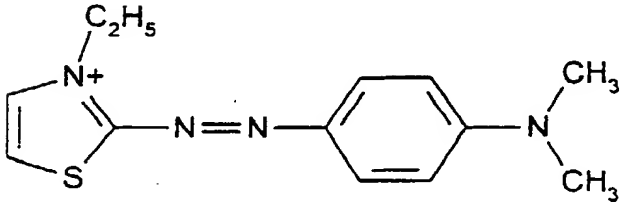
Cl^- (146)



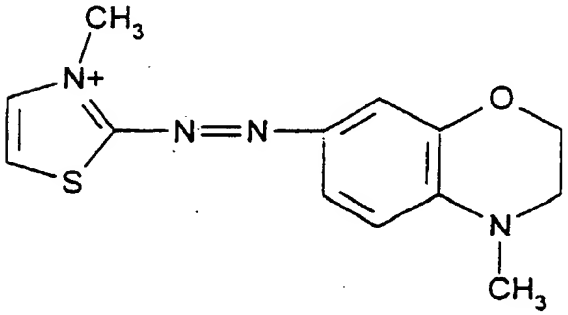
Cl^- (147)



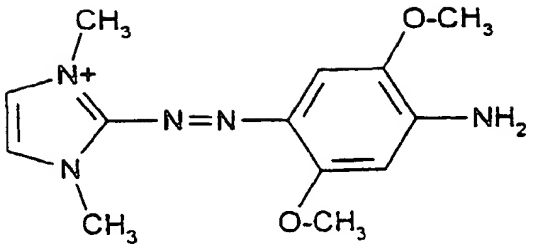
$CH_3SO_4^-$ (148)



$CH_3SO_4^-$ (149)

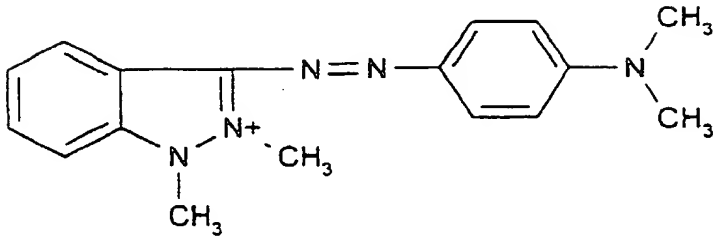


Cl^- (150)

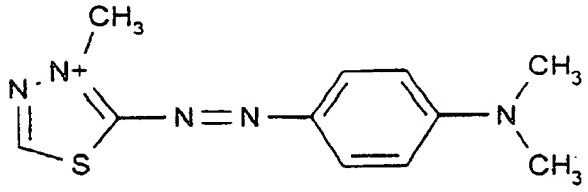


Cl^- (I51)

and

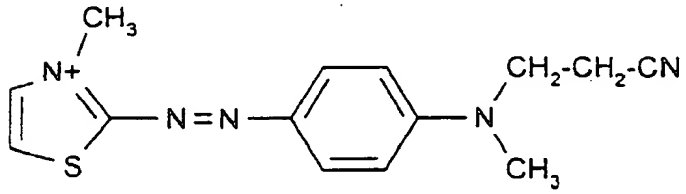


Cl^- (I52)



$CH_3SO_4^-$ (I53)

and

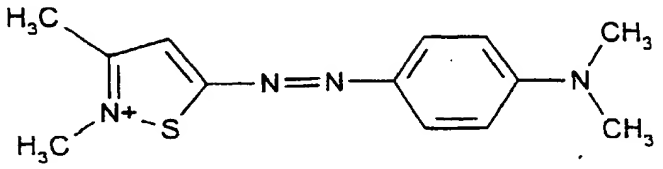


Cl^- (I54)

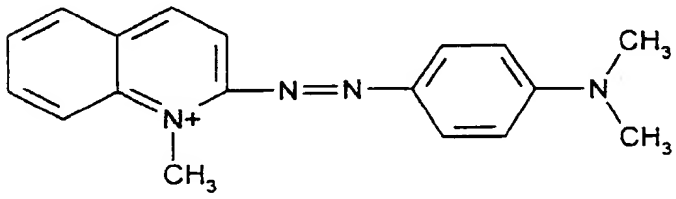
Among the compounds having the structures (I1) to (I54) which are described above, the compounds corresponding to the structures (I1), (I2), (I14) and (I31) are most particularly preferred.

Among the cationic direct dyes of formula (II) which can be used in the dyeing compositions in accordance with the invention, there may be mentioned

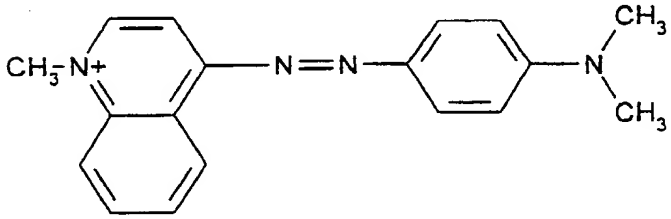
more particularly the compounds corresponding to the following structures (II1) to (II9):



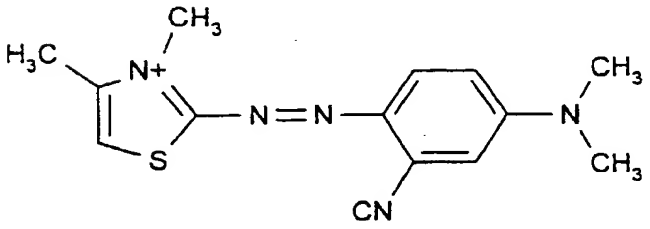
(II1)



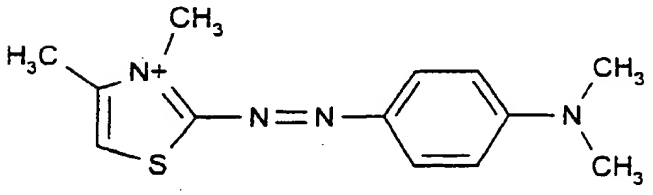
(II2)



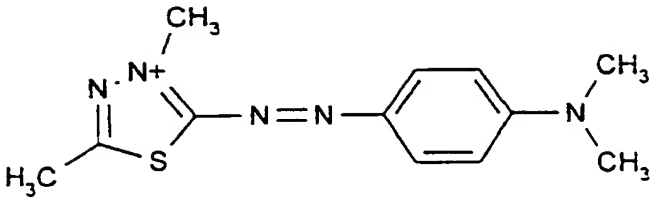
(II3)



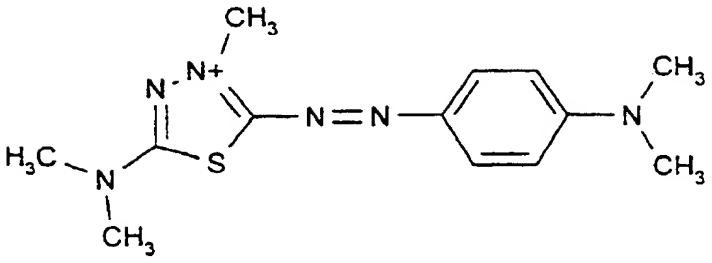
(II4)



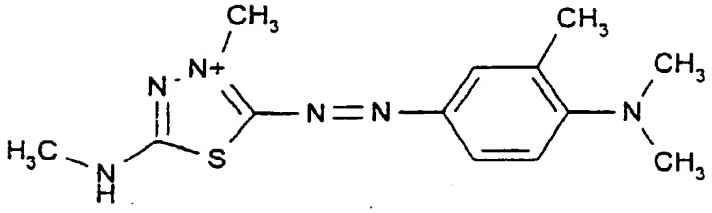
$CH_3SO_4^-$ (II5)



$CH_3SO_4^-$ (II6)

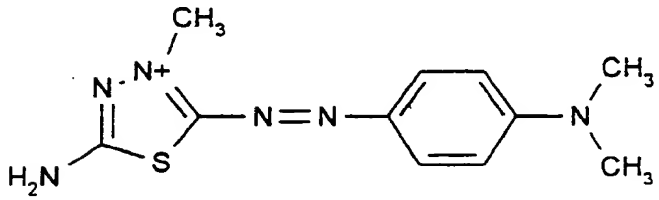


$CH_3SO_4^-$ (II7)



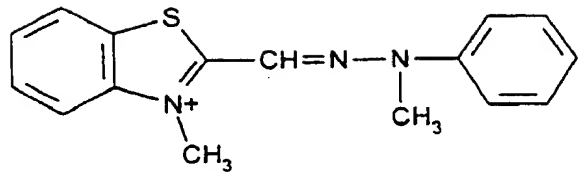
$CH_3SO_4^-$ (II8)

; and

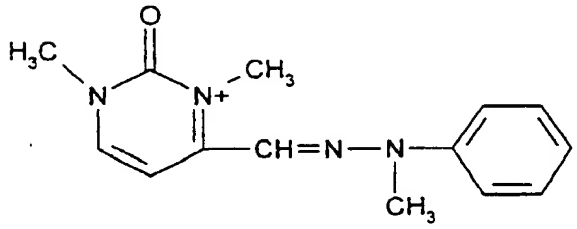


$CH_3SO_4^-$ (II9)

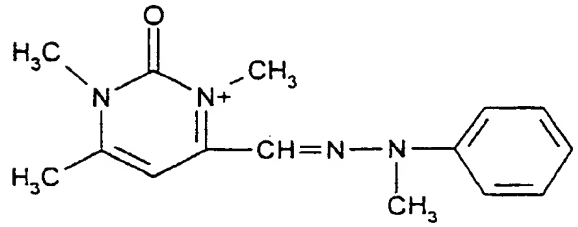
Among the cationic direct dyes of formula (III) which can be used in the dyeing compositions in accordance with the invention, there may be mentioned more particularly the compounds corresponding to the following structures (III1) to (III18):



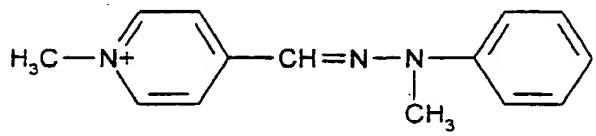
Cl^- (III1)



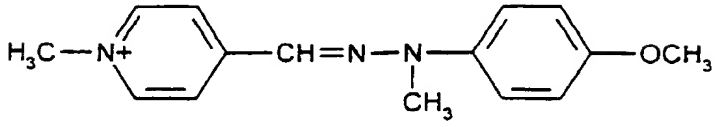
Cl^- (III2)



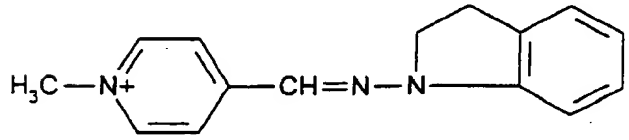
Cl^- (III3)



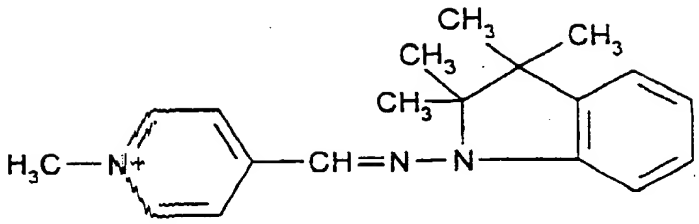
$CH_3SO_4^-$ (III4)



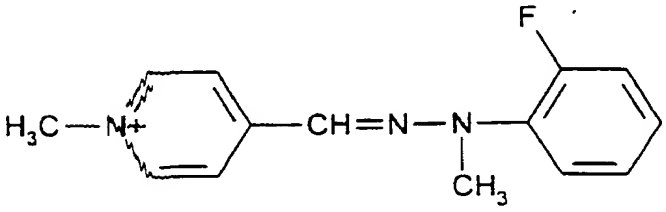
Cl^- (III5)



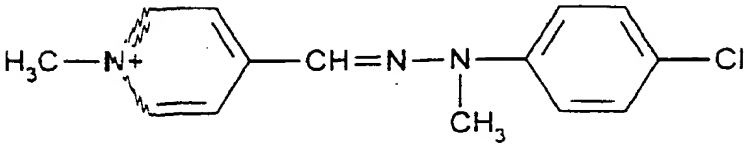
$CH_3SO_4^-$ (III6)



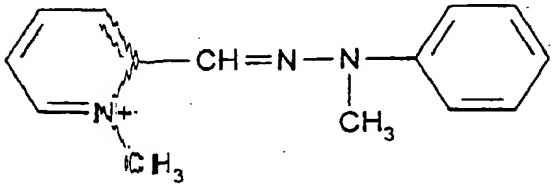
$CH_3SO_4^-$ (III7)



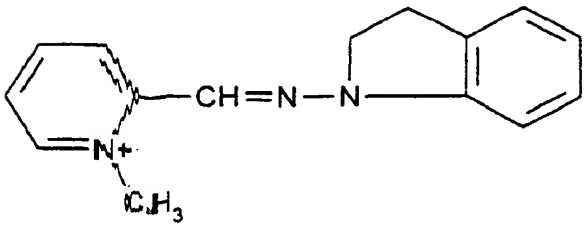
Cl^- (III8)



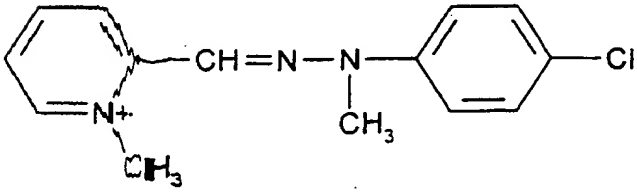
Cl^- (III9)



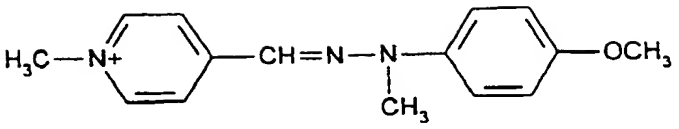
$CH_3SO_4^-$ (III10)



$CH_3SO_4^-$ (III11)

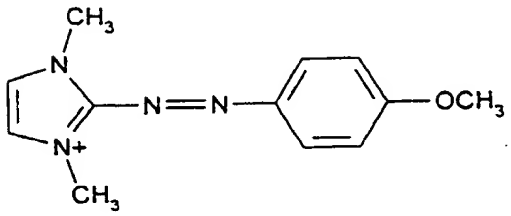


$CH_3SO_4^-$ (III12)



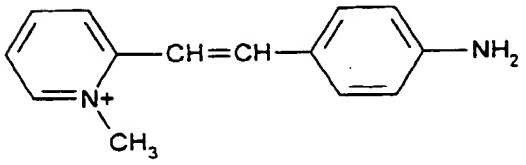
(III13)

;



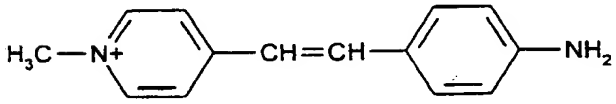
(III14)

;



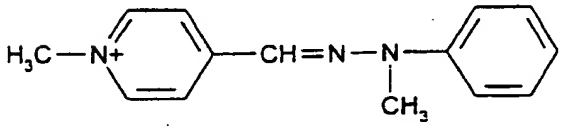
(III15)

;



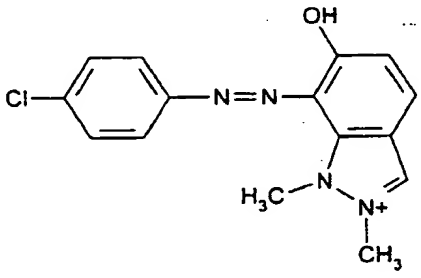
(III16)

;



(III17)

; and

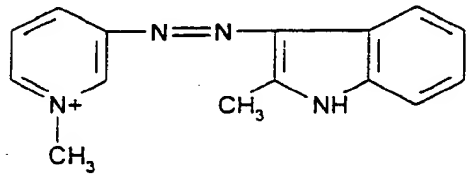


(III18)

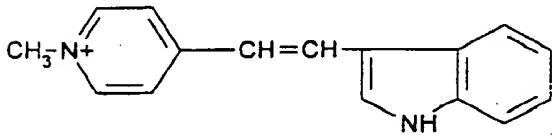
Among the particular compounds having the structures (III1) to (III18) which are described above,

the compounds corresponding to the structures (III4), (III5) and (III13) are most particularly preferred.

Among the cationic direct dyes of formula (III') which can be used in the dyeing compositions in accordance with the invention, there may be mentioned more particularly the compounds corresponding to the following structures (III'1) to (III'3):

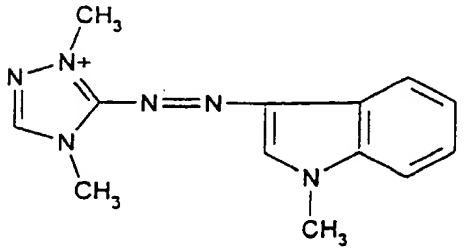


Cl⁻ (III'1)



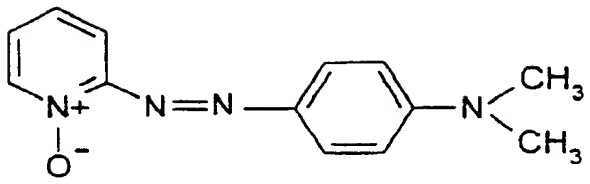
Cl⁻ (III'2)

; and

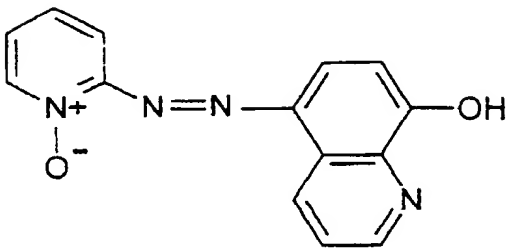


Cl⁻ (III'3)

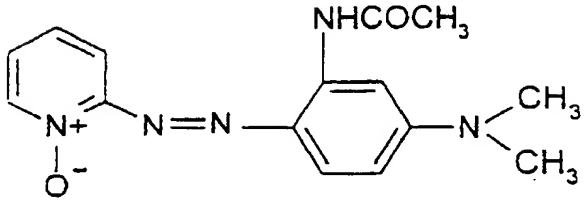
Among the cationic direct dyes of formula (IV) which can be used in the dyeing compositions in accordance with the invention, there may be mentioned more particularly the compounds having the following structures $(IV)_1$ to $(IV)_{77}$:



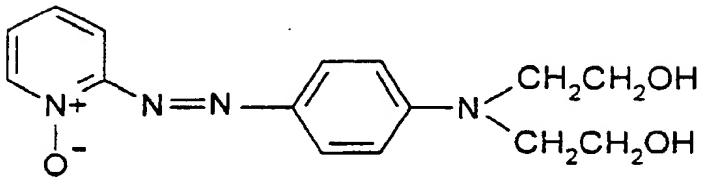
$(IV)_1$



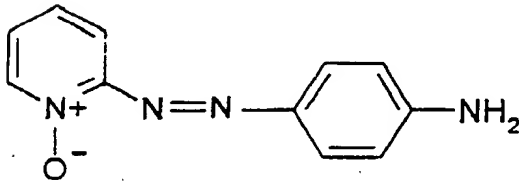
$(IV)_2$



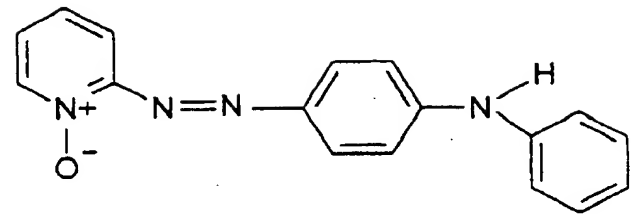
$(IV)_3$



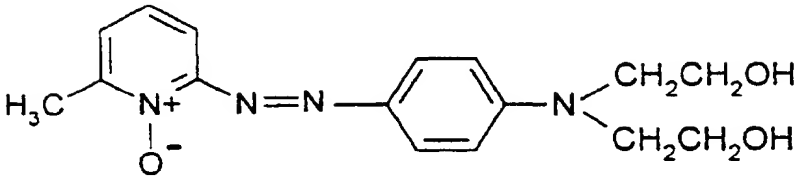
$(IV)_4$



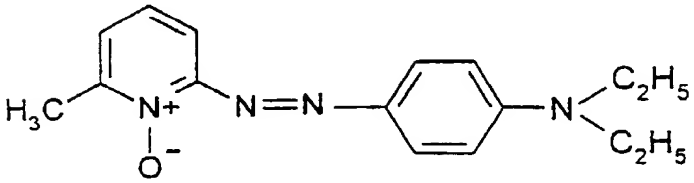
$(IV)_5$



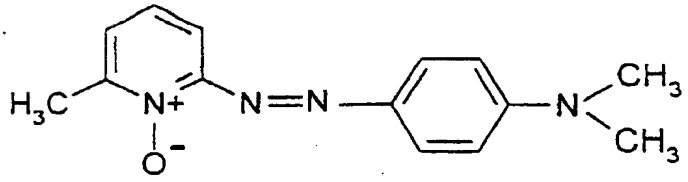
$(IV)_6$



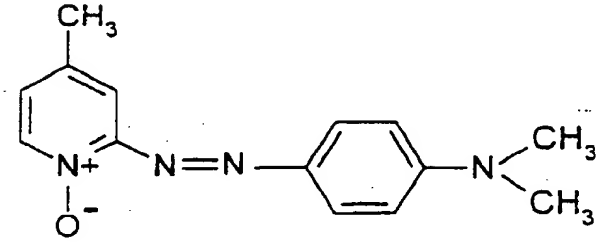
$(IV)_7$



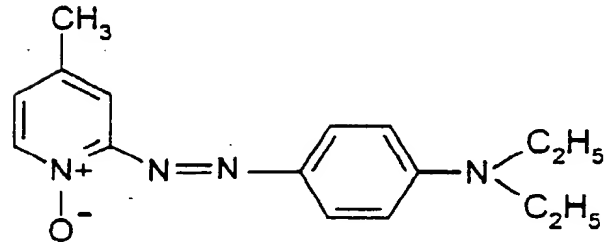
$(IV)_8$



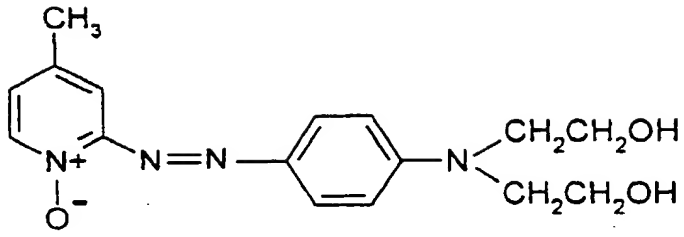
$(IV)_9$



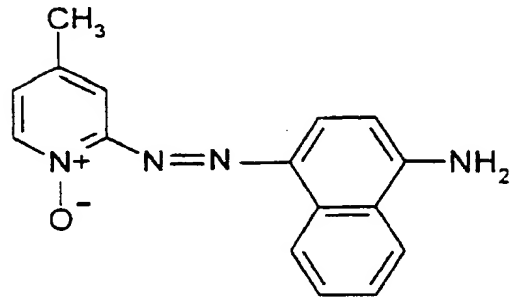
$(IV)_{10}$



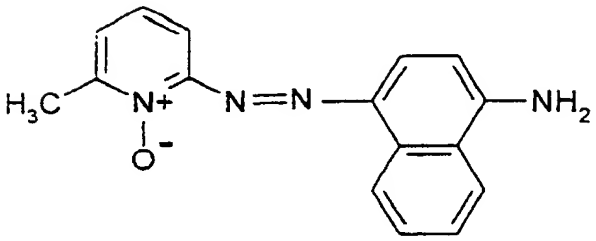
$(IV)_{11}$



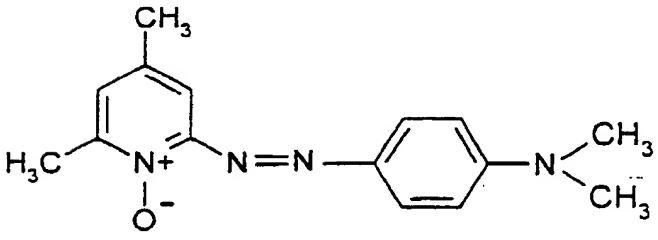
$(IV)_{12}$



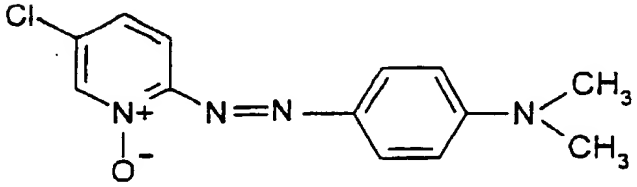
$(IV)_{13}$



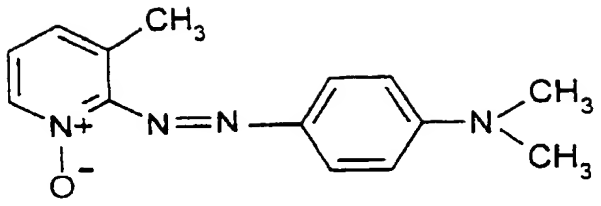
$(IV)_{14}$



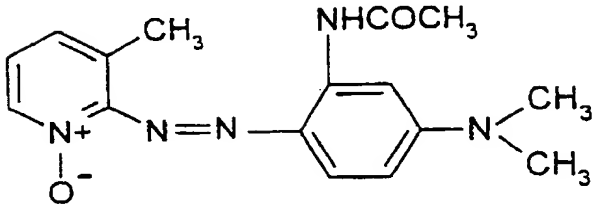
$(IV)_{15}$



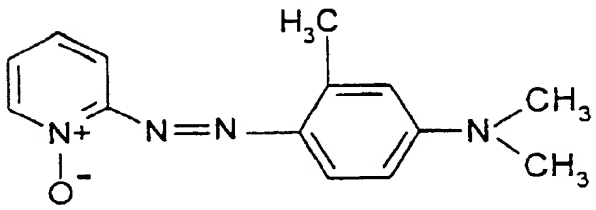
$(IV)_{16}$



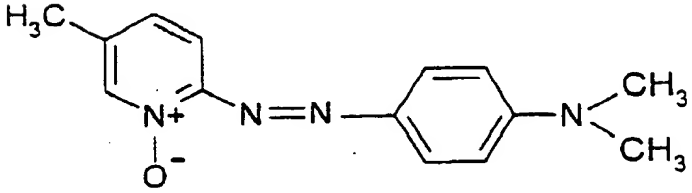
$(IV)_{17}$



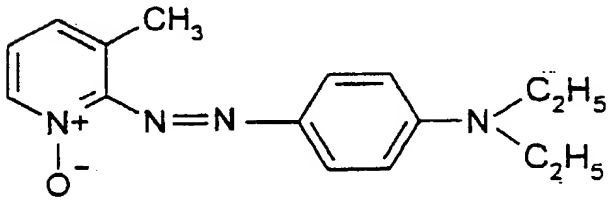
$(IV)_{18}$



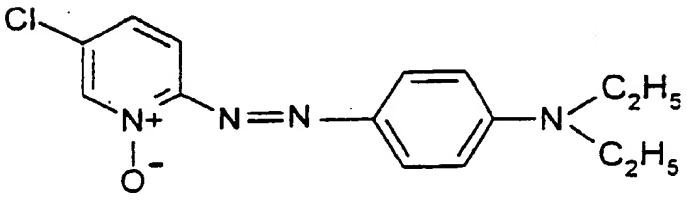
$(IV)_{19}$



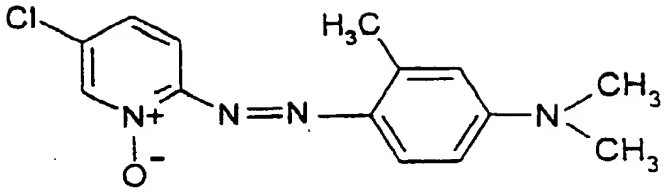
$(IV)_{20}$



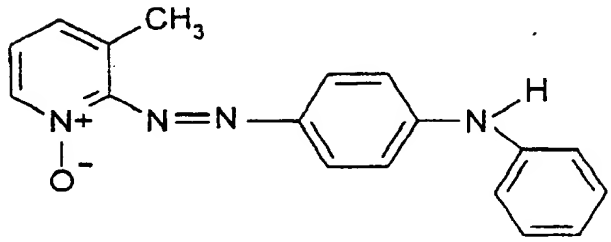
$(IV)_{21}$



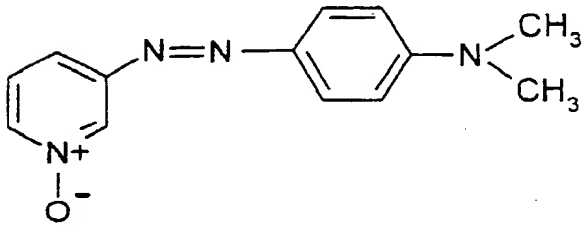
$(IV)_{22}$



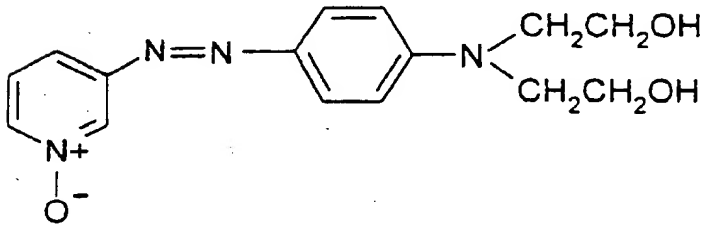
$(IV)_{23}$



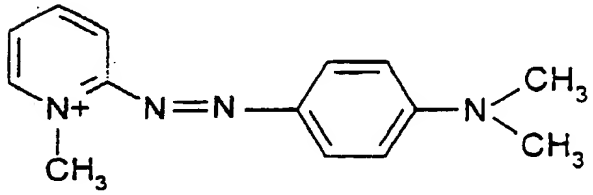
$(IV)_{24}$



$(IV)_{25}$

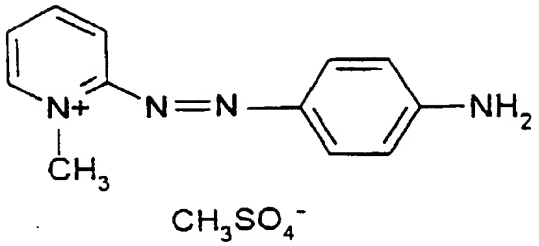


$(IV)_{26}$

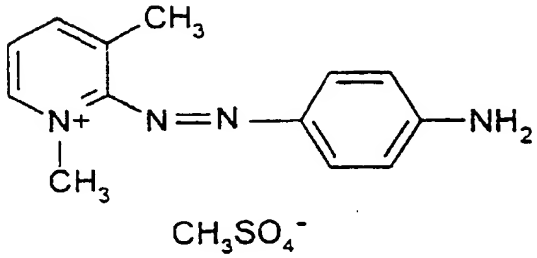


$CH_3SO_4^-$

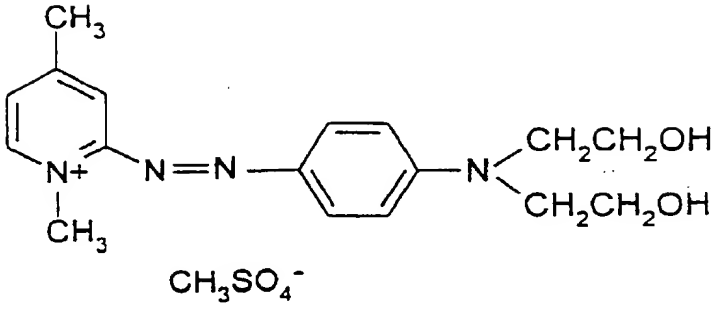
$(IV)_{27}$



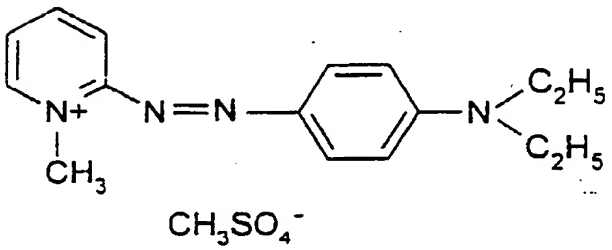
$(IV)_{28}$



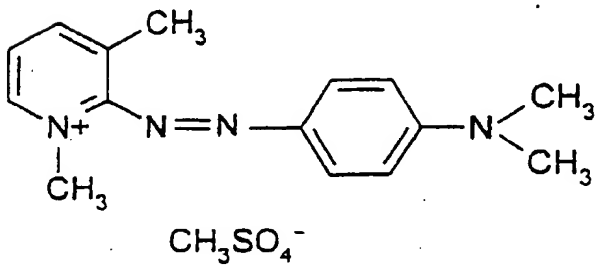
$(IV)_{29}$



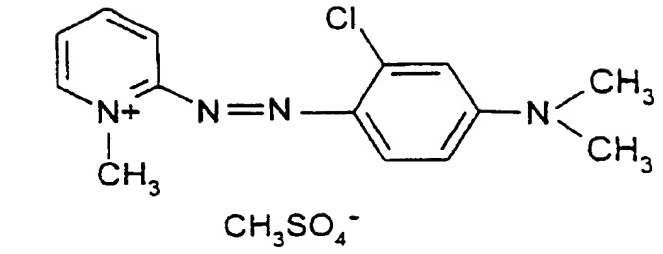
$(IV)_{30}$



$(IV)_{31}$

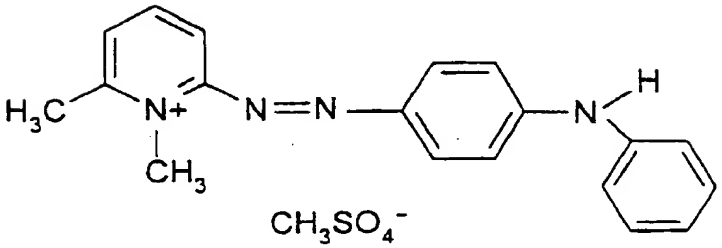


$(IV)_{32}$



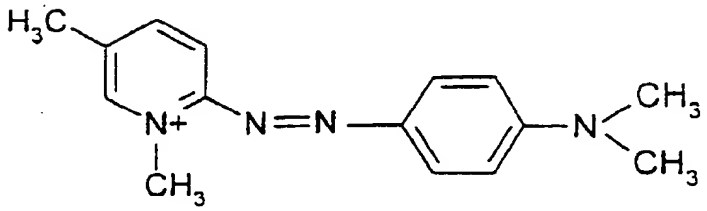
$CH_3SO_4^-$

$(IV)_{33}$



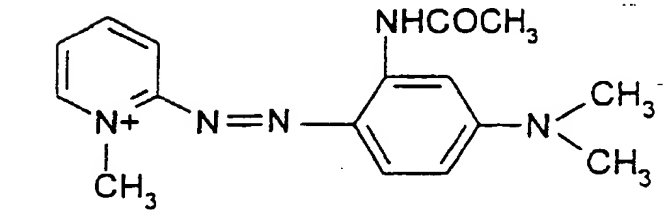
$CH_3SO_4^-$

$(IV)_{34}$



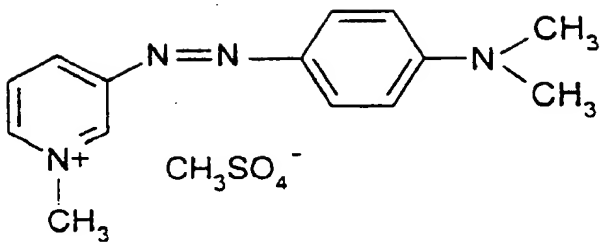
$CH_3SO_4^-$

$(IV)_{35}$

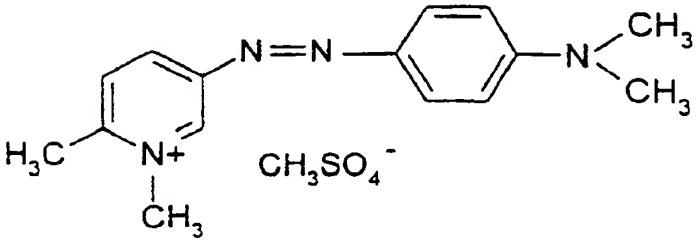


$CH_3SO_4^-$

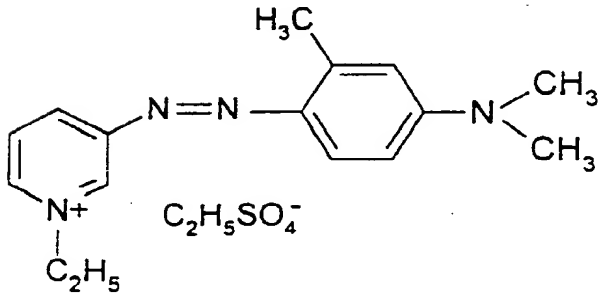
$(IV)_{36}$



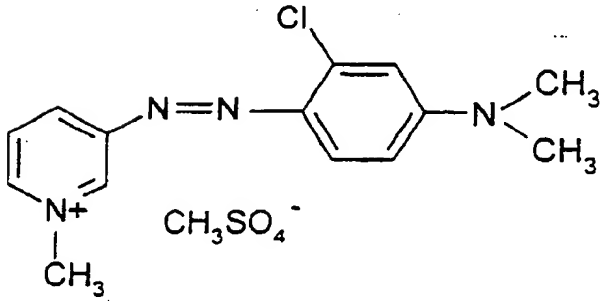
$(IV)_{37}$



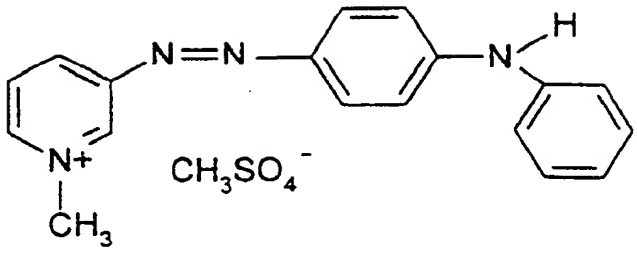
$(IV)_{38}$



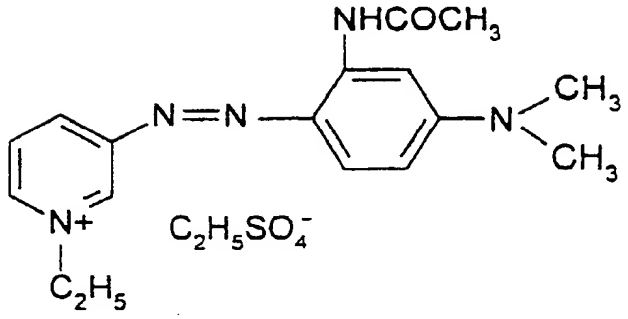
$(IV)_{39}$



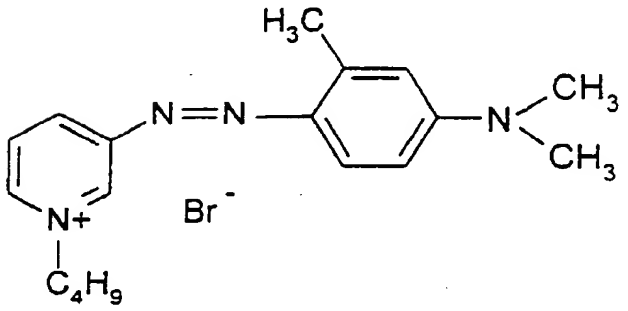
$(IV)_{40}$



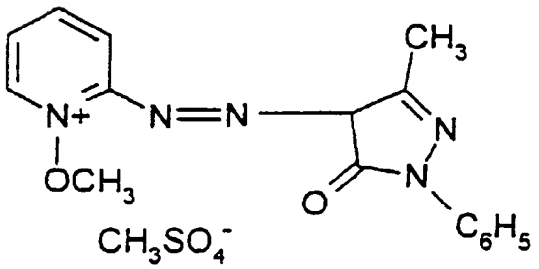
$(IV)_{41}$



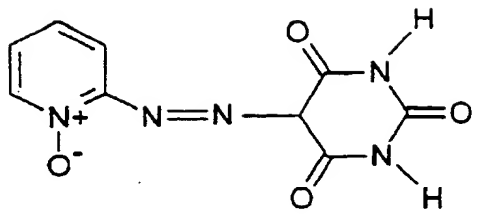
$(IV)_{42}$



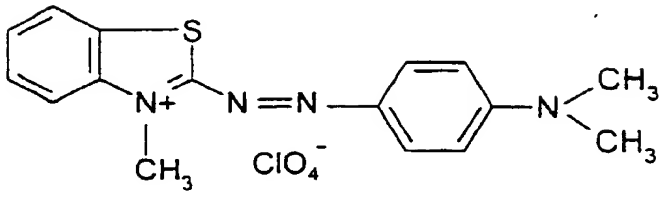
$(IV)_{43}$



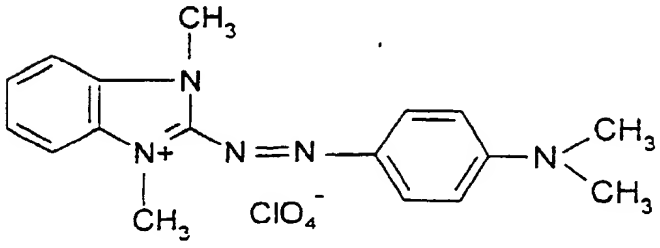
$(IV)_{44}$



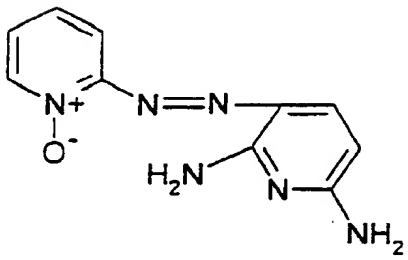
$(IV)_{45}$



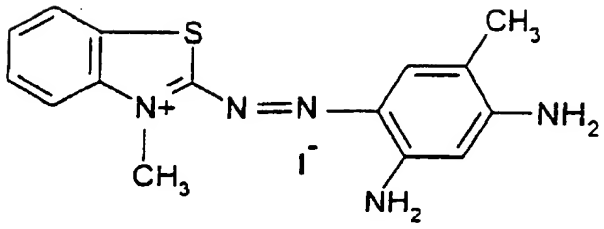
$(IV)_{46}$



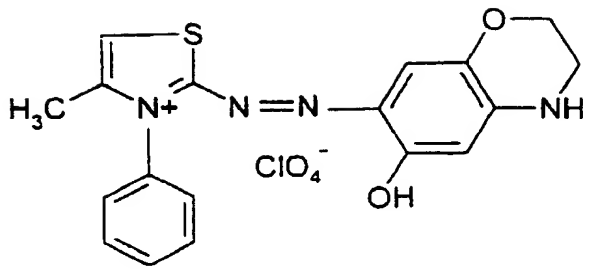
$(IV)_{47}$



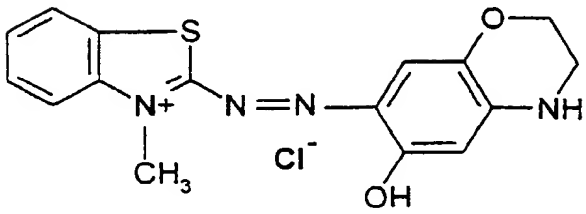
$(IV)_{48}$



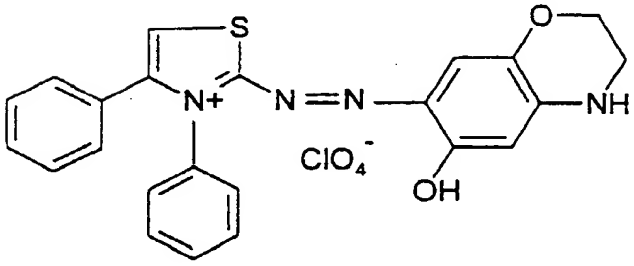
$(IV)_{49}$



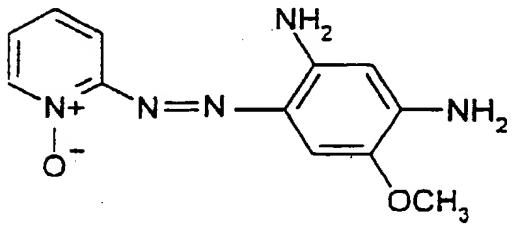
$(IV)_{50}$



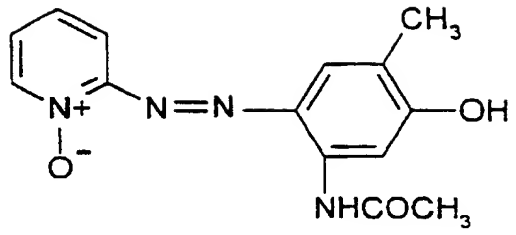
$(IV)_{51}$



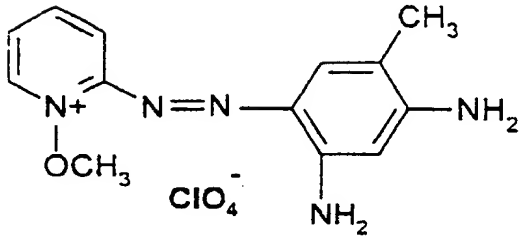
$(IV)_{52}$



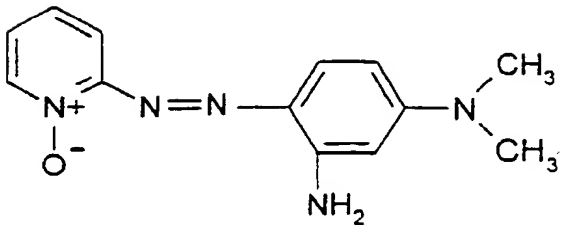
$(IV)_{53}$



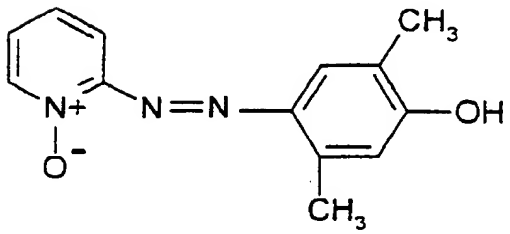
$(IV)_{54}$



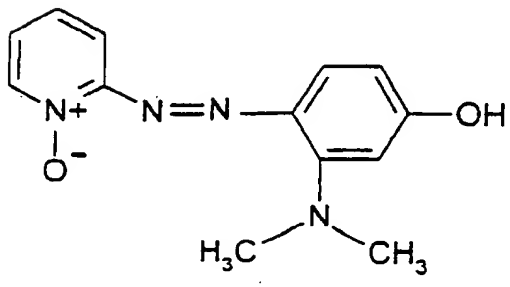
$(IV)_{55}$



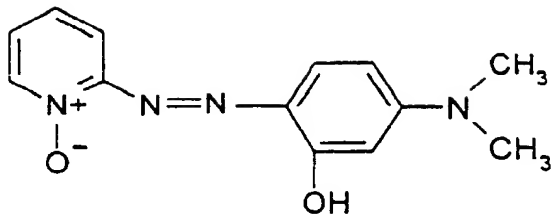
$(IV)_{56}$



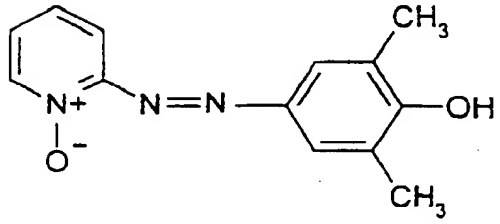
$(IV)_{57}$



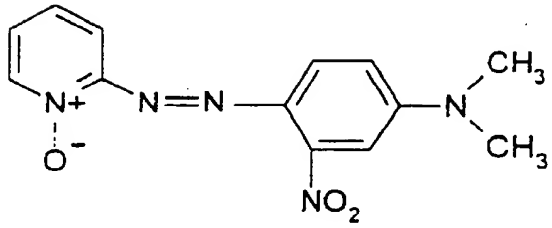
$(IV)_{58}$



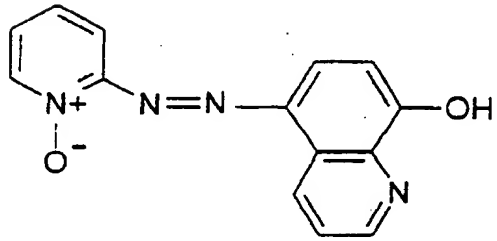
$(IV)_{59}$



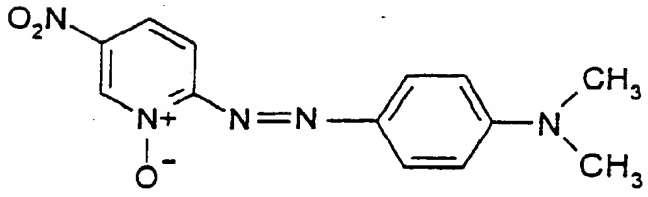
$(IV)_{60}$



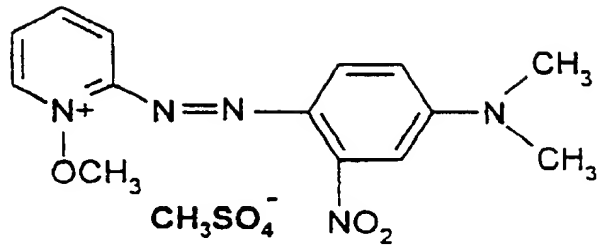
$(IV)_{61}$



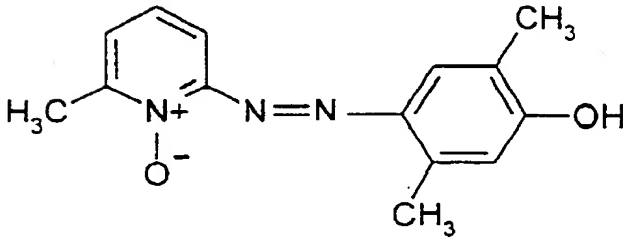
$(IV)_{62}$



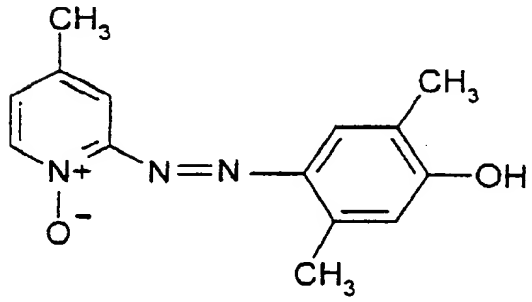
$(IV)_{63}$



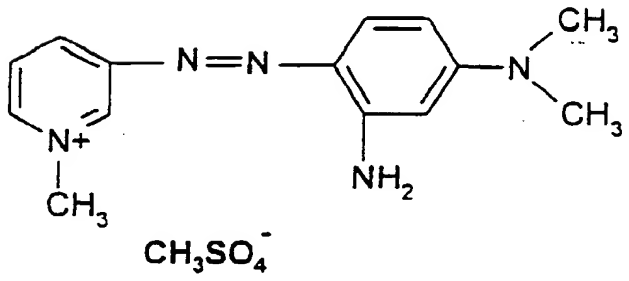
$(IV)_{64}$



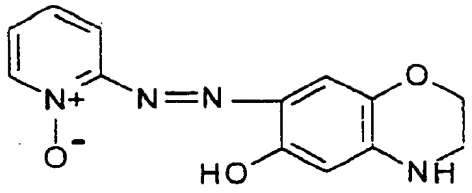
$(IV)_{65}$



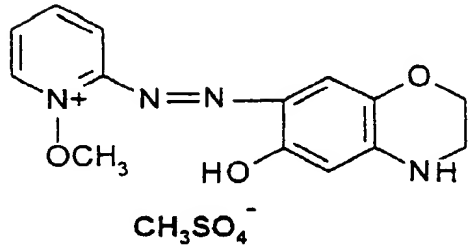
$(IV)_{66}$



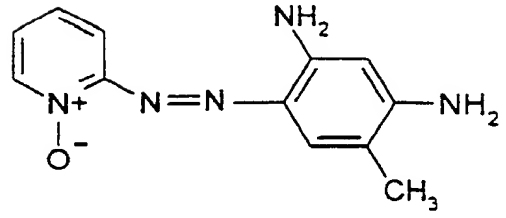
$(IV)_{67}$



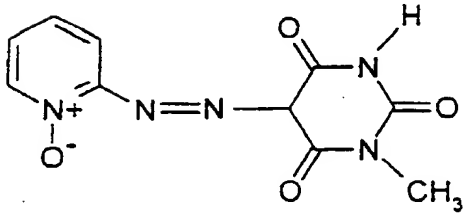
$(IV)_{68}$



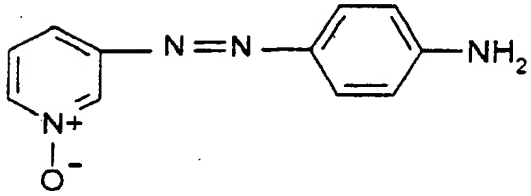
$(IV)_{69}$



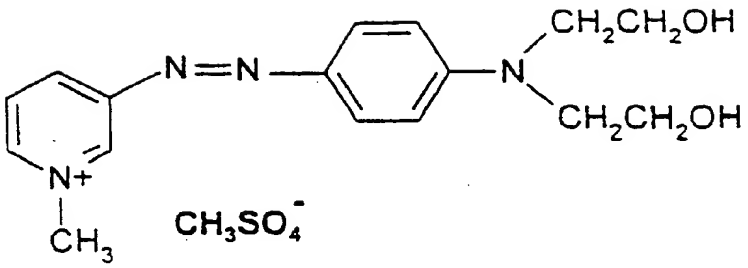
$(IV)_{70}$



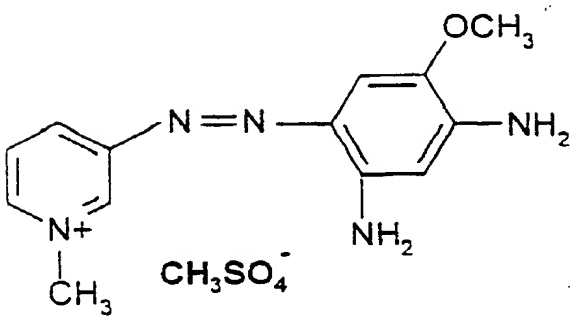
$(IV)_{71}$



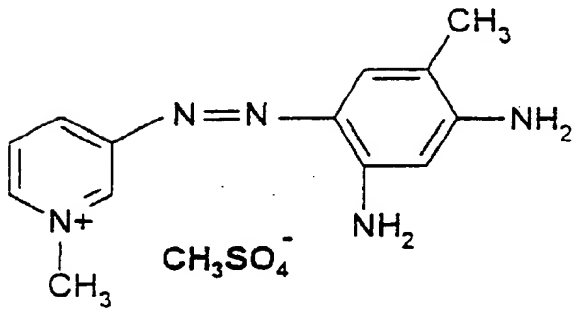
$(IV)_{72}$



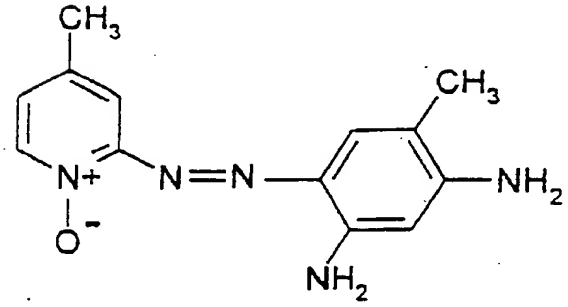
$(IV)_{73}$



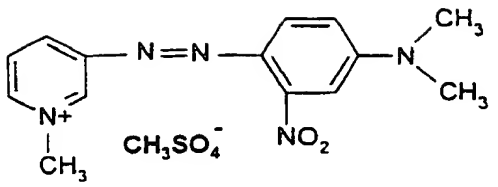
$(IV)_{74}$



$(IV)_{75}$



$(IV)_{76}$

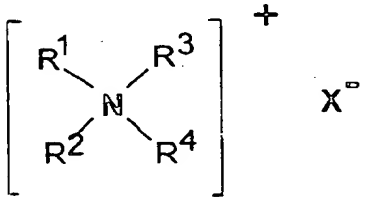


(IV)$_{77}$

The cationic direct dye(s) used according to the invention preferably represent from 0.001 to 10% by weight approximately of the total weight of the dyeing composition and still more preferably from 0.005 to 5% by weight approximately of this weight.

(ii) The quaternary ammonium salts which can be used according to the present invention are chosen from the group consisting of:

(ii)$_1$ - those of the following formula (V):



(V)

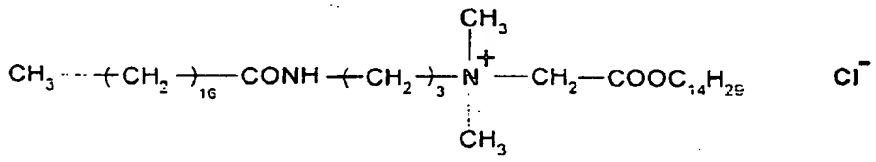
in which

the radicals R^1 and R^4, which are identical or different, denote a saturated or unsaturated, linear or branched, aliphatic hydrocarbon radical comprising from 1 to about 30 carbon atoms, or an alkoxy, alkoxycarbonylalkyl, polyoxyalkylene, alkylamido, alkylamidoalkyl, hydroxyalkyl, aromatic, aryl or alkylaryl radical comprising from about 12 to about 30 carbon atoms, with at

least one radical among R^1, R^2, R^3 and R^4 denoting a radical comprising from 8 to 30 carbon atoms;

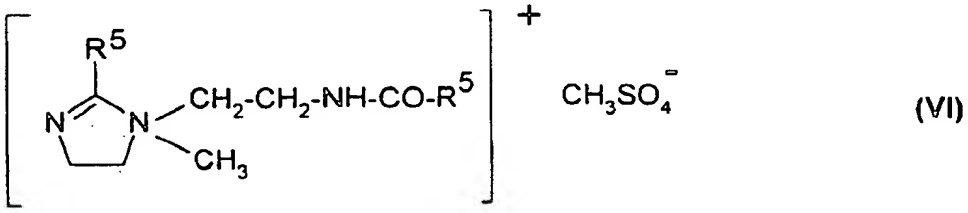
X^- is an anion chosen from the group comprising halides, phosphates, acetates, lactates and alkyl sulphates;

Among them, there may be mentioned, for example, (a) the dialkyldimethylammonium or alkyltrimethylammonium salts in which the alkyl radical comprises from about 12 to about 22 carbon atoms, such as the distearyldimethylammonium, cetyltrimethylammonium or behenyltrimethylammonium chlorides, (b) the di(C_1-C_2 alkyl)(C_{12}-C_{22} alkyl)hydroxy(C_1-C_2 alkyl)ammonium salts such as ~~oleocetylhydroxyethylammonium~~ chloride, or alternatively (c) the stearamidopropyldimethyl (myristyl acetate) ammonium chloride of formula:



sold under the trademark CERAPHYL 70 by the company VAN DYK.

(ii)$_2$ - the imidazolium salts of the following formula (VI):

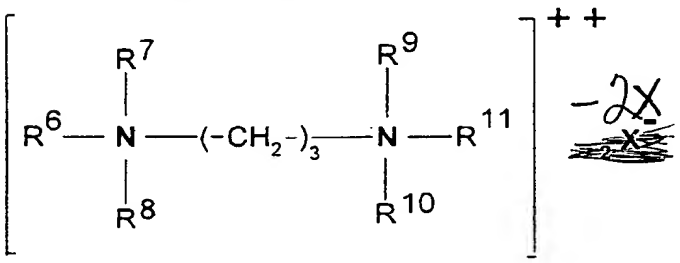


(VI)

in which,

R^5 is chosen from the alkenyl and/or alkyl radicals comprising from 13 to 31 carbon atoms and derived from tallow fatty acids, such as the product sold under the trademark "REWOQUAT W 7500" by the company REWO;

(ii)$_3$ - the quaternary diammonium salts of the following formula (VII):



(VII)

in which,

R^6 denotes an aliphatic radical comprising from about 16 to 30 carbon atoms, R^7, R^8, R^9, R^{10} and R^{11} are chosen from hydrogen or an alkyl radical comprising from 1 to 4 carbon atoms, and X^- is an anion chosen from the group comprising halides, acetates, phosphates and sulphates. Such quaternary diammonium salts comprise in particular propanetallowdiammonium dichloride.

According to the present invention, the quaternary ammonium salts of formula (V) are preferred in which R^1 to R^4, which are identical or different, denote alkyl or hydroxyalkyl radicals comprising from about 12 to about 22 carbon atoms, and in particular

behenyltrimethylammonium chloride, cetyltrimethylammonium chloride and oleocetyldimethylhydroxyethylammonium chloride.

The quaternary ammonium salt(s) (ii) used according to the invention preferably represent from 0.01 to 10% by weight approximately of the total weight of the dyeing composition and still more preferably from 0.05 to 5% by weight approximately of this weight.

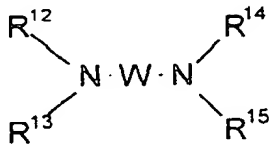
The appropriate dyeing medium (or carrier) generally consists of water or of a mixture of water and of at least one organic solvent for solubilizing the compounds which would not be sufficiently soluble in water. As organic solvent, there may be mentioned for example the C_1-C_4 lower alkanols such as ethanol and isopropanol, the aromatic alcohols such as benzyl alcohol as well as similar products and mixtures thereof.

The solvents may be present in proportions preferably of between 1 and 40% by weight approximately relative to the total weight of the dyeing composition, and still more preferably between 5 and 30% by weight approximately.

The pH of the dyeing composition in accordance with the invention is generally between 2 and 11 approximately, and preferably between 5 and 10 approximately. It may be adjusted to the desired value by means of acidifying or alkalinizing agents normally used in dyeing keratinous fibres.

Among the acidifying agents, there may be mentioned, by way of example, the inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid, lactic acid, sulphonic acids.

Among the alkalinizing agents, there may be mentioned, by way of example, aqueous ammonia, alkali metal carbonates, alkanolamines such as mono-, di- and triethanolamines as well as derivatives thereof, sodium or potassium hydroxides and the compounds having the following formula (VIII):



(VIII)

in which W is a propylene residue which is optionally substituted with a hydroxyl group or a C_1-C_6 alkyl radical; R^{12}, R^{13}, R^{14} and R^{15}, which are identical or different, represent a hydrogen atom, a C_1-C_6 alkyl radical or a C_1-C_6 hydroxyalkyl radical.

The dyeing composition in accordance with the invention may, in addition to the cationic direct dye(s) (i) defined above, contain one or more additional direct dyes which may for example be chosen from the nitrobenzene dyes, the anthraquinone dyes, the naphthoquinone dyes, the triarylmethane dyes, the xanthene dyes, the noncationic azo dyes.

When it is intended for oxidation dyeing, the dyeing composition in accordance with the invention contains, in addition to the cationic direct dye(s) (i), one or more oxidation bases chosen from the oxidation bases conventionally used for oxidation dyeing and among which there may be mentioned in particular the para-phenylenediamines, the bis-phenylalkylenediamines, the para-aminophenols, the ortho-aminophenols and the heterocyclic bases. When they are used, the oxidation base(s) preferably represent from 0.0005 to 12% by weight approximately of the total weight of the dyeing composition, and still more preferably from 0.005 to 6% by weight approximately of this weight.

When it is intended for oxidation dyeing, the dyeing composition in accordance with the invention may also contain, in addition to the cationic direct dye (i) and the quaternary ammonium salt (ii) as well as oxidation bases, one or more couplers so as to modify or increase the shimmer of the shades obtained using the cationic direct dye(s) (i) and the oxidation base(s).

The couplers which can be used in the dyeing composition in accordance with the invention may be chosen from the couplers conventionally used in oxidation dyeing and among which there may be mentioned in particular the meta-phenylenediamines, the meta-

aminophenols, the meta-diphenols and the heterocyclic couplers.

When they are present, the coupler(s) preferably represent from 0.0001 to 10% by weight approximately of the total weight of the dyeing composition and still more preferably from 0.005 to 5% by weight approximately of this weight.

The dyeing composition in accordance with the invention may also contain various adjuvants which are conventionally used in hair-dyeing compositions, such as antioxidants, penetrating agents, sequestrants, perfumes, buffers, dispersing agents, film-forming agents, ceramides, preservatives, screening agents and opacifying agents.

Of course, persons skilled in the art will be careful to choose this or these optional additional compounds such that the advantageous properties intrinsically attached to the dyeing composition in accordance with the invention are not, or not substantially, altered by the addition(s) envisaged.

The dyeing composition according to the invention may be provided in various forms, such as in the form of liquids, shampoos, creams, gels, or in any other form appropriate for dyeing keratinous fibres, and in particular human hair. It may be obtained by freshly mixing a composition, which is optionally pulverulent, containing the cationic direct dye(s) with a composition containing the quaternary ammonium salt.

When the combination of the cationic direct dye (i) and of the quaternary ammonium salt (ii) according to the invention is used in a composition intended for oxidation dyeing (one or more oxidation bases are then used, optionally in the presence of one or more couplers) or when it is used in a composition intended for direct lightening dyeing, then the dyeing composition in accordance with the invention contains, in addition, at least one oxidizing agent chosen for example from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such the perborates and persulphates, and enzymes such as peroxidases, laccases and oxidoreductases containing two electrons. The use of hydrogen peroxide or of enzymes is particularly preferred.

Another subject of the invention is a method of dyeing keratinous fibres and in particular human keratinous fibres such as hair using the dyeing composition as defined above.

According to a first variant of this dyeing method in accordance with the invention, at least one dyeing composition as defined above is applied to the fibres for a sufficient time to develop the desired colour, after which they are rinsed, optionally washed with shampoo, rinsed again and dried.

The time necessary for the development of the colour on the keratinous fibres is generally between 3

and 60 minutes and still more preferably 5 and 40 minutes.

According to a second variant of this dyeing method in accordance with the invention, at least one dyeing composition as defined above is applied to the fibres for a sufficient time to develop the desired colour, with no final rinsing.

According to a particular embodiment of this dyeing method, and when the dyeing composition in accordance with the invention contains at least one oxidation base and at least one oxidizing agent, the dyeing method comprises a preliminary stage consisting of storing in a separate form, on the one hand, a composition (A1) comprising, in an appropriate dyeing medium, at least one cationic direct dye (i) as defined above and at least one oxidation base and, on the other hand, a composition (B1) containing, in an appropriate dyeing medium, at least one oxidizing agent, and then mixing them at the time of use before applying this mixture to the keratinous fibres, the composition (A1) or the composition (B1) containing the quaternary ammonium salt (ii) as defined above.

According to another particular embodiment of this dyeing method, and when the dyeing composition in accordance with the invention contains at least one oxidizing agent, the dyeing method comprises a preliminary stage consisting of storing in a separate form, on the one hand, a composition (A2) comprising,

in an appropriate dyeing medium, at least one cationic direct dye (i) as defined above and, on the other hand, a composition (B2) containing, in an appropriate dyeing medium, at least one oxidizing agent, and then mixing them at the time of use before applying this mixture to the keratinous fibres, the composition (A2) or the composition (B2) containing the quaternary ammonium salt as defined above.

Another subject of the invention is a multicompartment device or dyeing "kit" or any other multicompartment packaging system in which a first compartment contains composition (A1) or (A2) as defined above and a second compartment contains composition (B1) or (B2) as defined above. These devices may be equipped with a means allowing the desired mixture to be delivered to the hair, such as the devices described in patent FR-2,586,913 in the applicant's name.

The following examples are intended to illustrate the invention without, however, limiting the scope thereof.

EXAMPLES

Examples 1 to 3:

The three direct dyeing compositions which are assembled in the following table were prepared:
(all contents expressed in grams)

EXAMPLES No. →	1	2	3
Cationic direct dye of formula (I1)	0.20		
Cationic direct dye of formula (I14)		0.20	
Cationic direct dye of formula $(IV)_{27}$			0.10
Oleocetyldimethylhydroxyethyl)-ammonium chloride	2.0 AS*		
Behenyltrimethylammonium chloride		2.0 AS*	
Cetyltrimethylammonium chloride			2.0 AS*
Ethanol	10	10	10
2-amino-2-methyl-1-propanol qs	pH 9	pH 9	pH 9
Demineralized water qs	100	100	100

AS* denotes Active Substance

The above compositions were each applied for 30 minutes to locks of natural grey hair which is 90% white. The hair locks were then rinsed, washed with a standard shampoo and then dried.

The locks were dyed in the following shades:

Examples	Shades obtained
1	dark red
2	dark orange
3	dark purple